Two Stage Synthesis of Aromatic Thioethers using Hydrogen Sulfide and Reusable Phase Transfer Catalyst

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Two Stage Synthesis of Aromatic Thioethers using Hydrogen Sulfide and Reusable Phase Transfer Catalyst

Dissertation submitted to the

National Institute of Technology Rourkela

In partial fulfillment of the requirements of the degree of

M.Tech (Research)

in

Chemical Engineering

by

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February 2017

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February 2, 2017

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This is to certify that the work presented in this dissertation entitled "**Two Stage Synthesis of Aromatic Thioethers using Hydrogen Sulfide and Reusable Phase Transfer Catalyst**" by "Preeti Jha ", Roll Number 614CH6005, is a record of original research carried out by her under my supervision and guidance in partial fulfillment of the requirements of the degree of *Master of Technology in Chemical Engineering*. Neither this dissertation nor any part of it has been submitted for any degree or diploma to any institute or university in India or abroad.

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Dedicated to My Family

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I, Preeti Jha, Roll Number 614CH6005 hereby declare that this dissertation entitled "Two Stage Synthesis of Aromatic Thioethers using Hydrogen Sulfide and Reusable Phase Transfer Catalyst " represents my original work carried out as a Master's student of NIT Rourkela and, to the best of my knowledge, it contains no material previously published or written by another person, nor any material presented for the award of any other degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the section "Bibliography". I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

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Acknowledgement

I wish to thank and express my heartfelt gratitude to my supervisor ***Dr. Sujit Sen,*** *Assistant Professor, Department of Chemical Engineering, National Institute of Technology Rourkela for guiding me to this interesting research work. I thank him for being for constantly motivating me through his valuable counsel as well as his excellent tips to build my research and writing skills.*

I would also like to thank my Master Scrutiny Committee members Prof. Santanu Paria (Associate Professor, Department of Chemical engineering), Prof. Sushmita Mishra (Associate Professor, Department of Chemical Engineering) and Prof. Aditya Kumar (Assistant Professor, Department of Chemical Engineering) for their helpful suggestions and discussions in developing my thesis.

I wish to convey my sincere gratitude to the Director, NIT- Rourkela for providing me the opportunity to pursue my research in this Institute.

I am also thankful to all lab mates, Ujjal Mondal, Gaurav Singh, Sivamani, Devipriya Gogoi, Saroj Kumari, Pratik Mishra and Tatinaidu Kella for their time-to-time help, encouragement and creating an excellence atmosphere both inside and outside the department.

I am obliged to all my friends Rubi Kumari, Anuradha Kumari, Manisha Maharana, Sakira begum, Sourabhya, Grusha Arora and Preeti Kumari for their friendships and encouragements. I cannot be what I am, without the blessings of my father Sudhakar Jha and support of my sisters Mrs. Sujata Jha Mishra, Mrs Reshma Jha Shenoy and Miss Kavita Jha to whom I shall give all the credit for my existence and the position I'm in now.

Lastly, I wish to thank my loving mother Late Madhavi Jha, whose blessings always give me strength to overcome all obstacles and difficulties in my life.

Preeti Jha

Abstract

This present investigation is based on the idea of using waste sulfur compound i.e. Hydrogen Sulfide (H_2S) which is unutilized byproduct of industries like petroleum and natural gas processing industries. This proposed work comprises of two stages: firstly, conventional absorption of H_2S in the absorbent alkanolamines like methyldiethanolamine (MDEA) which is selective towards hydrogen sulfide. This H_2S-rich MDEA solution has been proposed to act as a sulfiding agent for aromatic halides to synthesize aromatic thioether which is a fine chemical used in photographic emulsions, high pressure lubricants and additive as anti-wear in motor oil and has application in various anticorrosive formulations. The objective is to synthesize the aromatic thioether like Bis-(p-chlorobenzyl) Sulfide) using reactant aromatic halides like (p-chlorobenzyl chloride) and H_2S rich aqueous alkanolamines (e.g. MEA, MDEA etc.). For this double phasic reaction was carried out in presence or absence of solvent like toluene as well as insoluble phase transfer catalyst are being used. This present work is carried out using tributylmethylammonium chloride-polymer bound, tributylmethylphosphonium chloride-polymer bound and Amberlite IR-400 as the insoluble catalysts which were further reused for betterment of the economy of the project. So the study was carried out in three phases. The initial experiments shows encouraging results with 100% conversion of reactant p-chlorobenzylchloride in the solvent toluene, 100% selectivity of the desired product Bis-(p-chlorobenzyl) sulfide) and the catalyst was reused up to 3 times. A generalized empirical kinetic model was developed and successfully validated against the experimental results. In the second phase of study, Response surface methodology accompanied with Central composite design was used for the study of the reaction kinetics, model development and the optimization of the reaction conditions. In the third phase study, solvent free synthesis of Bis-(p-chlorobenzyl) Sulfide) was carried out. This whole investigation is oriented towards a green technology for utilizing toxic H_2S under waste management approach.

Keywords: Hydrogen Sulfide; Dibenzyl Sulfide; Bis-(p-chlorobenzyl) Sulfide methyldiethanolamine; monoethanolamine; Phase Transfer Catalyst; Selectivity; Kinetic modeling; Response surface methodology, Central composite design.

Contents

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Nomenclature

S^{2-}	Sulfide anion
S_2^{2-}	Disulfide anion
Q^+	Catalyst cation
QSQ	Catalyst active intermediate
QSH	Catalyst active intermediate

Abbreviation

MDEA	N-Methyldiethanolamine
MEA	Monoethanolamine
TEA	Triethanolamine
DEA	Diethanolamine
DIPA	Diisopropanolamine
BC	Benzyl chloride
DBS	Dibenzyl sulfide
p-CBC	para- Chlorobenzyl Chloride
p-CBM	para- Chlorobenzyl Mercaptan
BPCBS	Bis-(para-Chlorobenzyl) Sulfide

CHAPTER 1

Introduction

1.1. Nature of hydrogen sulfide

Hydrogen sulfide, aka sour gas, swamp gas, manure gas, is a chemical compound with formula H_2S. It is a colorless, extremely hazardous, and flammable gas with "rotten egg" like characteristic odor. It is heavier than air, and hence it accumulates in lower lying areas which are poorly ventilated, enclosed like manure pits, sewer lines, manholes, basements, and underground telephone vaults. It is a highly flammable gas, and air-H_2S gas mixture can be explosive. It travels to the area of ignition and burns with a characteristic blue flame to produce toxic gas or vapors (SO_2). It is soluble in water to produce weak acid (hydrosulfuric or sulfhydric acid) (Chou 2003).

1.2. Effect of H_2S on human health and equipment

Effect of H_2S on human health depends on the time of exposure and concentration of H_2S. It acts as an irritant with effect on oxygen utilization capacity of the human body as well as on the central nervous system. At lower concentration, it irritates eye, throat, nose and respiratory system (e.g. cough, shortness of breathing burning/tearing of eyes, etc.) whereas prolong exposure of the gas may lead to headache irritability, insomnia, digestive disturbances and weight loss. At moderate concentration (200-300 ppm), it causes respiration irritation, vomiting, staggering and excitability. Whereas high concentration (700 ppm) of hydrogen sulfide lead to rapid unconsciousness, shock, inability to breath, coma, pulmonary paralysis, sudden collapse or ultimately death (Syed et al. 2006).

The presence of H_2S in tail-gas streams of many industries is not desirable because of its corrosive nature. For example, in mild steel pipelines in oil and natural gas industries, H_2S reacts with the iron to form an iron sulfide layer on the pipeline, and that layer produces a lot of toxic vapors and gasses like SO_2 upon combustion. There are many other detrimental problems caused by the gas such as an increase in the process pressure requirements, increase in the gas compressor capacity, deactivation of catalysts, undesired side reactions, etc. (Haniblin 1973).

1.3. Sources of hydrogen sulfide in the environment

Most of the H_2S emission in the atmosphere has a natural origin (~ 90%). This gas mainly occurs around lakes, springs and geothermally active area. Volcanos and saline marshes are leading sources of H_2S. Hydrogen sulfide is a major compound in the natural sulfur cycle (Fig 1.1). Some bacteria produce H_2S by the decay of plant and animal protein.

Bacteria, fungi, and some Actinomycetes release this gas into the environment during the decay of compounds containing sulfur-bearing amino acids.

Petroleum refineries and natural gas treatment plants are the industries which are accountable for large H_2S emission into the environment. Crude natural gas, refinery gas, and biogas carry contamination of H_2S gas. Upon oxidation of these gasses, H_2S oxidize to form sulfur dioxide which is a strong air pollutant (contributes to acid rain). So due to the sweetening of these gasses, H_2S is produced as a by-product. Some other industries that are responsible for H_2S emission are kraft pulp & paper manufacturing industry, carbon disulfide production plants, and viscous rayon industry.

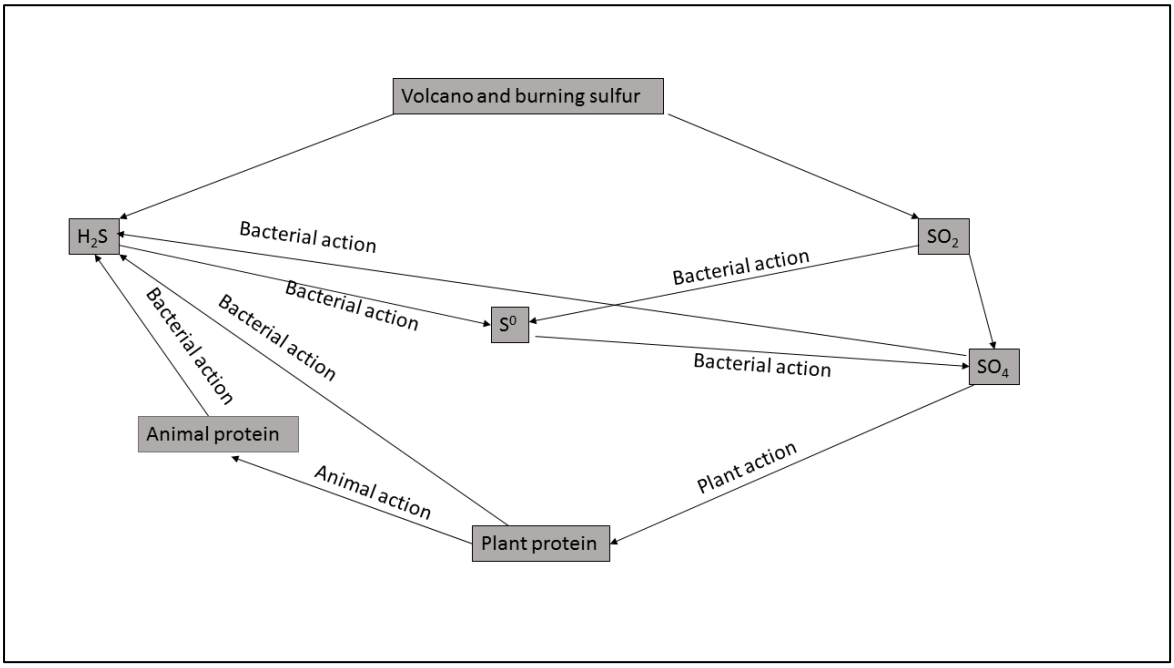


Fig 1.1. Sulfur Cycle

1.4. Process of removal of H_2S from the environment

H_2S gas is present in high concentrations in the gaseous streams of petroleum refineries, gas treatment plants, paper & pulp industries and biogas treatment plants. It leads to several problems like corrosion of equipment (pipelines, compressors, engines and gas storage tanks), strong poisoning of reformer catalyst and fuel cells. Thus, it is recommended to bring down the level of H_2S in the gas streams to prevent the equipment from corrosion and catalysts from poisoning. Based on some mass transfer mechanism like absorption and adsorption, the sour gas can be removed from its streams. For adsorption, activated carbon, molecular sieves, Oxides of Zinc & Iron and alkaline solids can be used.

As H_2S is sparingly soluble in water, using water scrubbing also the H_2S gas can be separated from biogas. Because of its acidic nature, it is soluble in ammonia and alkanolamines. Membrane purification, bio-filters, bio-trickling filters, and bio-scrubbers are also recently being used for H_2S removal.

1.4.1. Absorption and scrubbing

For H_2S removal from gaseous streams, absorption can be either physical or chemical. For physical absorption, H_2S is removed by absorption in water or other solvents such as methanol, ethers of polyethylene glycol whereas in chemisorption, water solubility can be enhanced by making the water alkaline or by oxidation of H_2S to the alkaline water or by oxidation of H_2S to more water soluble compounds. As H_2S is a weak acid, so it is soluble in alkaline water.

Chemisorption is also helpful in H_2S removal using amines, alkanolamines, and other solvents. Absorption by oxidation with iron or zinc oxide slurry has been replaced by chelated iron based process. The advantage of the process is the high-efficiency removal of H_2S (up to 99%) and ability to handle a wide range of pollutant.

1.4.1.1. Water scrubbing

Water Scrubbing is the process of washing sour gas with pressurized water flow. It removes the acid gas contaminants from the gas mixture by a significant value. Even though CO_2 is less soluble in the water than H_2S, selective absorptive removal of H_2S is still unachieved. The water used for the scrubbing can be reused and recirculated. The water to be used for cleaning can also be brought from the waste water treatment plant, but it may lead to bacterial growth in the vessels and pipelines. Thus, proper cleaning is an inseparable part of the process. The water consumption decreases up to 100 times when water is reused and recirculated. The used water needs to be properly treated before discharging into the environment (Lien et al. 2014).

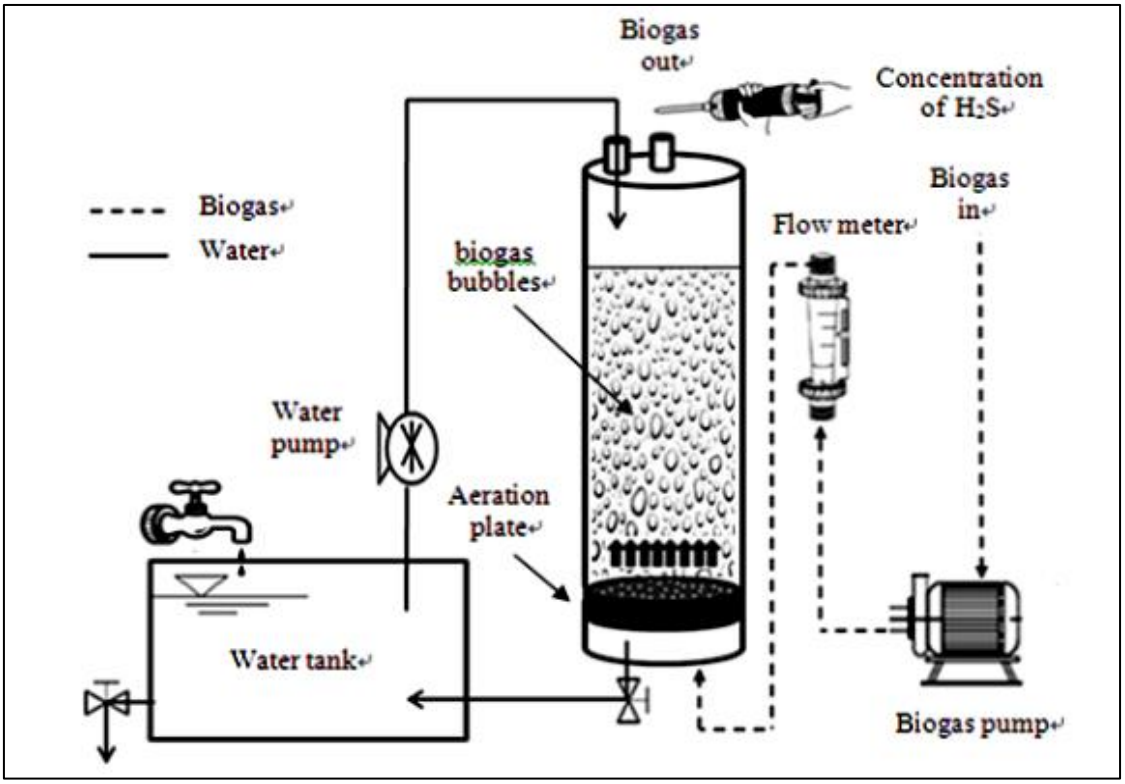


Fig 1.2. Schematic of desulfurization of biogas using water scrubbing (Lien et al. 2014)

1.4.1.2. Physical absorption

The physical absorption technology is same as the water washing but instead of water; other solvents are also used. The organic solvents that can be used for better selective absorption of H_2S are methanol, propylene carbonate, and ether of polyethylene glycol. Genosorb is a well-known commercial solvent, mainly constituted of polyglycolic diethyl ethers and used in a process name as so-called Selexol process. The process was not found competitive in the selective H_2S removal from natural gas streams, but it is applicable where mere upgrading to relatively pure methane is desired. The process is economically interesting and useful for very high gas flows.

1.4.1.3. Chemical absorption

Chemisorption is also helpful in H_2S removal using amines, alkanolamines, and other solvents. Absorption by oxidation with iron or zinc oxide slurry has been replaced by chelated iron based process. The advantage of the process is the high-efficiency removal of H_2S (up to 99%) and ability to handle a wide range of pollutant.

1.4.1.3.1. Ammonia based process

For H_2S removal, aqueous ammonia had been a well-accepted approach (Hamblin 1973; Harvey and Makrides 1980). The process is appealing because both the chemicals used in the process come from the plant itself. During the scrubbing process, the reaction occurring between ammonia, hydrogen sulfide and water has been represented by the following equations (Scheme 1.1)

$$NH_3 + H_2O \rightarrow NH_4OH \quad (1.1)$$

$$2NH_3 + H_2S \rightarrow NH_4HS \quad (1.2)$$

$$NH_3 + H_2O \rightarrow (NH_4)_2S \quad (1.3)$$

Scheme 1.1. Basic Reaction of aqueous ammonia with hydrogen sulfide

In the recent years, the popularity of ammonia-based process of H_2S removal in diminishing. But still, some coke oven plants are using the process for desulfurization of the COG (coke oven gas).

Disadvantages:

- High partial pressure of ammonia because of low vapor pressure
- Problems in the regeneration of aqueous ammonia as the regeneration process also requires soluble catalyst like hydroquinone which contaminates the sulfur product with catalyst
- High ammonia loss per scrubbing cycle
- Extensive corrosive nature of ammonia

1.4.1.3.2. Alkanolamines based processes

A number of alkanolamines have been used for H_2S removal by various petroleum refineries and chemical industries. The process has numerous advantages over an amine-based process like low-pressure, flexible operating conditions like temperature and concentration of alkanolamine. The industrially relevant alkanolamines that have been commercially used for H_2S removal are listed below in Fig. 1.3.

Aqueous Monoethanolamine (MEA) and Diethanolamine (DEA) are mostly used for acid gas capture and utilization of various sources. MEA comes with various advantages

like high reactivity, low solvent cost, ease of reclamation, low molecular weight (result in high solution capacity at moderate concentration) but suffers from several shortcomings like poor selectivity towards H_2S, highly corrosive nature, high energy requirement of regeneration and formation of irreversible side products upon the reaction with CS_2. DEA is less corrosive as compared to MEA.

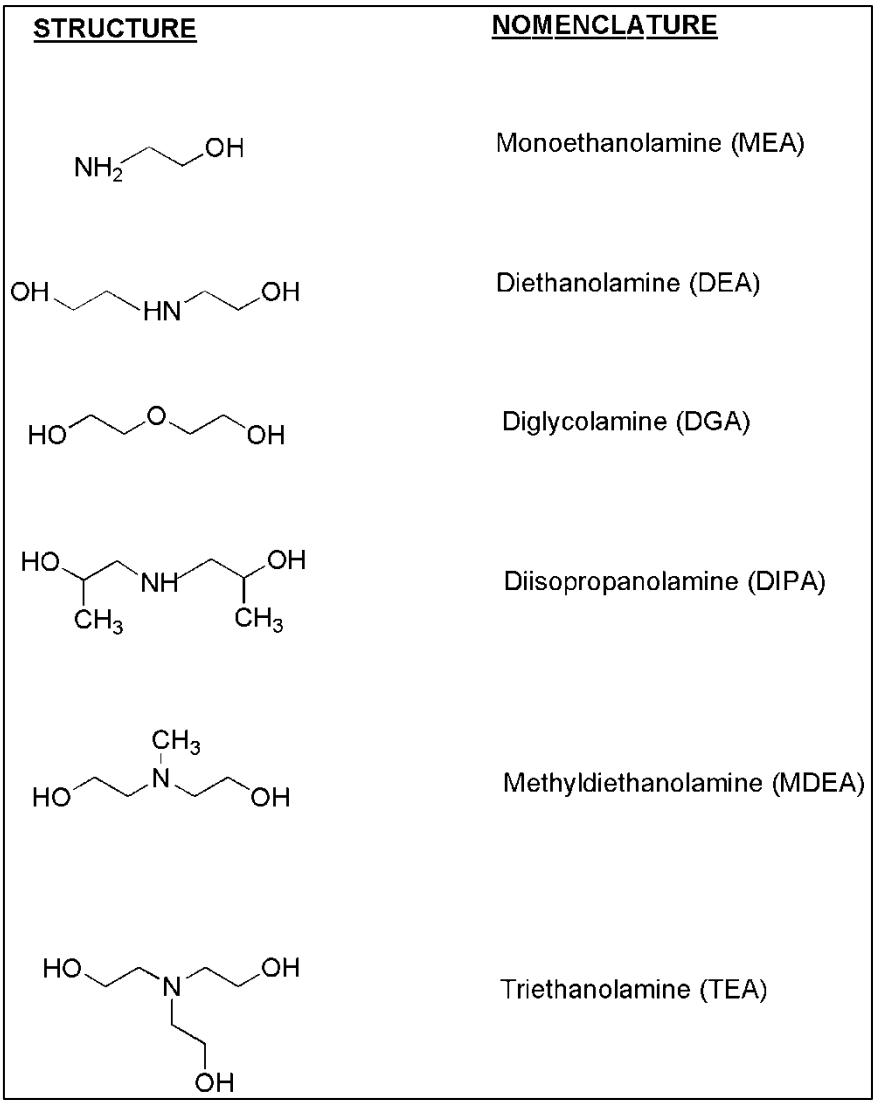


Fig.1.3. Alkaonolamines and their structure

Triethanolamine (TEA) is out of those alkanolamines that were firstly used for H_2S and CO_2 gas removal from gas streams. TEA is accompanied with advantages like a high rate of reaction acid gasses. Sweetening of acid gas can be improved by using TEA spread over silica gel. Later TEA was replaced by MEA and DEA because of its lower molecular weight and capability of more effective H_2S removal.

Diglycolamine (DGA) can also be employed for the absorption of sour gas as it has many advantages like low vapor pressure, the high ambient temperature of operation, less capital cost, easy reclamation and less initial investment and operating cost but it has less selectivity towards H_2S as compared to MDEA.

Diisopropanolamine (DIPA), as H_2S absorbent, has benefits like other polluting gasses can also be absorbed using the same absorbent hence less selective towards H_2S, and less steam is required for the reclamation through steam distillation.

Methydiethanolamine (MDEA) is replacing the other absorbents nowadays as it has many advantages like low vapor pressure, easy recovery and high selectivity towards H_2S.

1.4.2. Chemical reaction based/biological process based removal

The sour gas hydrogen sulfide can be removed by means of some chemical reactions or biological methods. The oxidation of hydrogen sulfide using some catalyst, reaction with some Iron salts or simple biological process were proved to be helpful for the removal of H_2S. The descriptive explanation of the different process is written as follows.

Catalytic oxidation of hydrogen sulfide

In this process, catalytic oxidation of H_2S to sulfur takes place without the formation of sulfur oxide, in the presence of a metal-chelated catalyst and soluble alkali metal or alkaline earth metal or ammonia or amine salt of an acid. The acid should be lying in the pH range of 1.2 to 6.

The catalytic oxidation of H_2S to elemental sulfur in the presence of a polyvalent metal chelate catalyst solution is represented by the Eq. (1.4) (redox reaction).

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \tag{1.4}$$

Reaction of H_2S with iron salts/oxides

Biogas is highly contaminated with H_2S gas. This method is very effective in the reduction of H_2S gas to a high level but meagerly effective in attaining a low level of H_2S, i.e., in the range of vehicle and injection into the gas grid demands. From this process, H_2S concentration can be brought down to 200-100 ppm. Thus, the method is a partial H_2S removal process.

In this process, iron chlorides, oxides, and phosphates are charged to the digester slurry or into the feed substrate in a pre-storage tank. Ferric Chloride ($FeCl_3$) can be charged along with iron hydroxide ($Fe(OH)_3$ or $Fe(OH)_2$) in solid form. The reaction of iron salts with H_2S is shown in Scheme 1.2 to form insoluble ferrous sulfide salt. The precipitation prevents the stripping of H_2S in biogas.

Ferrous chloride:

$$Fe^{+2} + S^{-2} \rightarrow FeS \quad (1.5)$$

Ferrous hydroxides:

$$2Fe(OH)_3 + H_2S \rightarrow 2Fe(OH)_2 + S + 2H_2S \quad (1.6)$$

$$Fe(OH)_2 + H_2S \rightarrow FeS + 2H_2O \quad (1.7)$$

Ferric chloride:

$$2FeCl_3 + 3H_2S \rightarrow 2FeS\downarrow + S\downarrow + 6HCl \quad (1.8)$$

Scheme 1.2. Reaction of iron salts with hydrogen sulfide

Biological reduction of H_2S

This is the simplest method of desulfurization of biogas. In this process, oxygen or air is directly passed through biogas in anaerobic digestion of the storage tank. Same as a natural sulfur cycle, here also sulfates to elemental sulfur is converted by following the biological pathway, i.e., by *Thiobacillus bacteria*, which grow on the surface of digestor and offers necessary microaerophilic surface.

The process claims to lower the H_2S level up to 80-99% under specific temperature and the reaction time.

Advantages:

The process is cheaper and easily maintainable.

Disadvantages:

The necessity to supply oxygen leads to the anaerobic fermentation process. Thus, fermentation gets disturbed, and methane formation takes place. Hence, lowers the yield of elemental sulfur production.

- Yellow clusters of sulfur are deposited on the surface, and it increases chances of corrosion.
- Need of control over air/O_2 supply to avoid the explosion.
- Accumulation of O_2 and N_2 in the biogas stream.

1.5. Utilization of H_2S

There is various industrial based process available for H_2S removal and utilization like Claus, LO-CAT, MINICAT, Sulferox, Sulfothane, etc. these processes are widely accepted for H_2S utilization but suffers from a major disadvantage that all the process leads to the formation of elemental sulfur. So the amount of sulfur being produced by the processes mentioned above is higher than the consumption of the sulfur. Thus, the researchers are thinking about an alternative solution.

1.5.1. Claus process

It is the most significant and industrially adopted process of elemental sulfur production from H_2S. It was invented by an English scientist, Carl Friedrich Claus in 1883. Firstly, the H_2S is absorbed in the amine using amine treatment plants secondly the H_2S-rich amine along with O_2 is passed through the pre-heated catalyst bed. The product recovered in the process are Sulfur, water, and thermal energy.

The feed for Claus process unit originates from acid gas sweetening plant. In the process unit, there are two steps thermal and catalytic. In the thermal step combustion of H_2S laden gas at very high temperature (1000-1400 ^{0}C). The step is a highly exothermic reaction and leads to the formation of SO_2. The second step is catalytic where H_2S reacts with SO_2 to produce elemental sulfur.

Disadvantages:

- High temperature requirement of the process
- Requirement of exact process control over the ratio of oxygen to H_2S in the feed
- Loss of valuable hydrogen energy in the process

1.5.2. LO-CAT (Catalytic scrubbing)

The process is wet cleaning, liquid redox system that uses a chelated iron solution to convert H_2S to elemental sulfur. It is applicable for all gaseous stream, e.g., natural gas, air, amine acid gas, refinery fuel, landfills, bio fills, biogas, etc. flexibility of the operation

allows up to 100% turndown in H_2S concentration and gas flow. As suggested by its name, it utilizes less catalyst. Hence, the process proves to be more reliable, efficient and economical.

It has been accepted in many industrial processes for e.g. biogas from an anaerobic digester, oil and gas production CO_2 purification, geothermal steam production, landfills gas, air ventilation treatments, coke oven gas desulfurization. There are three types of LO-CAT processes (Fig. 1.4) - aerobic, anaerobic and auto-circulation process. Aerobic process design is primarily used for odor control; anaerobic process design is used to remove H_2S from anaerobic gas streams or when product recovery is required, and auto-circulation process gives a cost effective treatment of anaerobic non-explosive gas streams. The process causes low consumption of catalyst.

1.5.3. MINI-CAT

The basic chemistry behind MINI-CAT process is same as that of LO-CAT process as it has originated from LO-CAT process. As compared to LO-CAT process, it has less capacity of the sulfur load. Due to this, the capital cost of the MINI-CAT plant is less than LO-CAT and is found to be cost effective in removing H_2S from various sources like municipal waste, landfills, and biogas treatment. It reduces the chemicals cost up to 80%. The operating time substantially reduces in the case of MINICAT process.

1.5.4. SulFerox

A redox-based process used for converting hydrogen sulfide to elemental sulfur by reacting H_2S with the aqueous ferric ion. Essential steps of the process are absorption, regeneration, and sulfur recovery. The process description is given below:

I. Absorption- sour gas stream comes into contact with liquid soluble irons (iii) and H_2S gets selectivity oxidation to elemental sulfur.
II. Regeneration: it involves reoxidation of iron (ii) to maintain active ion supply, i.e., iron (iii).
III. To maximize the recovery of sulfur, the elemental sulfur formed in the first reaction is concentrated and filtered out.
IV. The filtrate is recycled back to maximize the ferric solution recovery. The process offers savings in the capital cost and operating costs by removing H_2S directly to elemental sulfur.

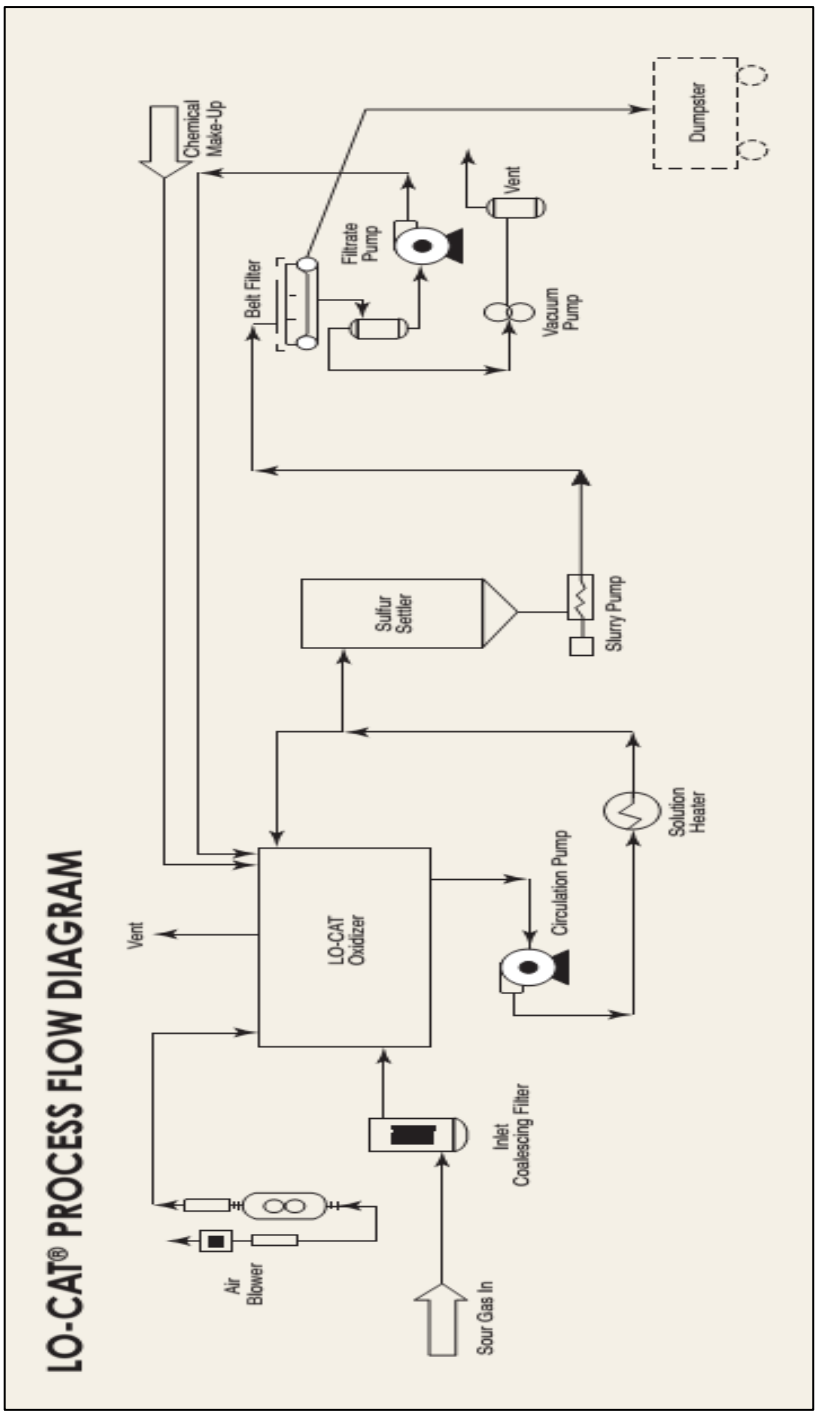


Fig 1.4. LO-CAT Schematic diagram

1.5.5. Sulfothane

Sulfothane is an industrially important process of H_2S capture and utilization. It consists of two steps and resembles a chemical alkaline scrubbing process. The alkaline washing process. The alkaline solution is NaOH solution which is regenerated by a biological process using aerobic bacteria *Thiobacillus.* The reaction is represented by the following equations.

$$H_2S + NaOH \rightarrow NaHS + H_2O \quad (1.9)$$

$$NaHS + 1/2O_2 \rightarrow S\downarrow + H_2O \quad (1.10)$$

The second equation represents a biological process in which sodium sulfide is oxidized to elemental sulfur. The process is environmentally safe with minimal power requirement. It is clogging free, so no maintenance is required. The process is operated in the ambient conditions in terms of temperature and pressure. The chemical requirement of the process is very less.

1.6. Knowledge gap

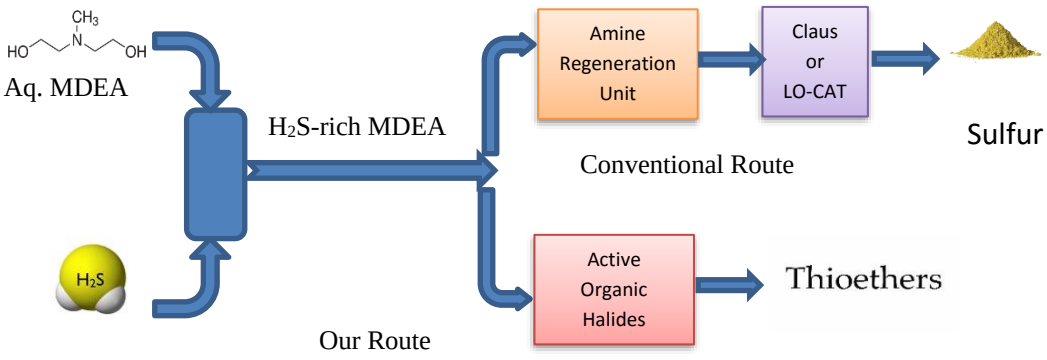
Ammonium hydroxide was used by Hamblin in 1973 for the removal of H_2S from the gas stream. Triethanolamine (TEA), monoethanolamine (MEA), diethanolamine (DEA), Diisopropanolamine (DIPA) and N-methyldiethanolamine (MDEA) have come into existence later on for absorptive removal of H_2S in industry. Nowadays MDEA is replacing the other absorbent because of its better selectivity towards the H_2S in the presence of CO_2. Therefore the present work has been carried out using MDEA for the absorption of H_2S gas, and H_2S laden MDEA has been used for the synthesis of value-added fine chemicals like bis-(p-chlorobenzyl) Sulfide.

DBS has earlier been synthesized from benzyl chloride using tetrahexylammonium bromide as phase transfer catalyst (PTC). Reduction of sulfoxide using Al-$NiCl_2$-$6H_2O$ as reducing agents was also performed for the synthesis of DBS. But due to long reaction time, expensive reagents and extreme reaction conditions, the reduction is not found to be an economical method. All of the catalysts used so far for the synthesis of thioethers like DBS are soluble in nature and therefore it very difficult to reclaim it back and reuse. In the case of L-L PTC, disposal of the used catalyst is also an issue because of its hazardous nature.

So, in the field of utilization of H_2S for the synthesis of thioethers like BPCBS, the use of a reusable polymer-supported catalyst is still awaited. In this case, polymer-supported PTC is a 'green' option because of its insoluble nature and therefore, it is easy to reclaim and environment-friendly. In this type of PTC (also known as triphase L-L-S catalyst), the catalyst is impregnated on some polymers like polystyrene and polyacrylamide. The support can either be soluble or insoluble as well. Ambelite IRA-400 has been used as L-L-S PTC for the synthesis of dibenzyl disulfide by Singh.

1.7. Methodology of the present work

The present methodology adopts a two stage reaction protocol: in the first stage, we follow the same industrial techniques in chemisorption of hydrogen sulfide in aqueous MDEA solution; and in the second stage, we design an alternative path to conventional H_2S utilization (Claus, LO-CAT, etc.), i.e., using the H_2S-rich MDEA solution as sulfiding agent to carry out Williamson-type synthesis protocol to yield thioethers from active benzyl halides. The present route is proposed to yield value-added fine chemicals, i.e., thioethers in place of elemental sulfur obtained from conventional processes. Also as we can see from the Scheme, it required one-step less as compared to conventional step. The alternative scheme is presented below:



Scheme 1.3. Methodology of Present Work

1.8. Objective of the present work

The current work encloses the capturing of H_2S, which is a poisonous gas coming from waste streams of a petroleum refinery, hydrotreating plants, paper and pulp industries

etc., through its selective absorption in suitable absorbents like methyldiethanolamine (MDEA) and its utilization in the synthesis of aromatic thioether using in the presence of reusable phase transfer catalyst. The present investigation comprises of following objectives:

a) Study of the kinetics of the synthesis of bis-(p-chlorobenzyl) sulfide using H_2S rich MDEA, p-chlorobenzyl chloride in the presence of toluene as solvent and reusable polymer-supported catalyst tributylmethylammonium chloride and development of the empirical kinetic model and its validation against the experimental data.
b) Dual optimization of the reaction parameter for maximization conversion of p-CBC and product selectivity.
c) Solvent-free synthesis of bis-(p-chlorobenzyl) sulfide using H_2S-rich MDEA and p-chlorobenzyl chloride in the presence of reusable polymer-supported catalyst Amberlite IR-400.

1.9. Multiphase reaction and phase transfer catalyst

The preliminary requirement of a molecular reaction to take place is a collision between the reacting molecules. No other conditions like time, external agitation, energy quantity, may help the rate of reaction until the two molecules come into contact. As reported by Stark in 1871, despite continuous agitation for several days the reaction of two molecules with different phases doesn't reach to any extent. There are several examples of such reactions where reactive species are present as two phases. Thus, a technique called "*phase transfer catalysis*" offers a method to avoid the use of a solvent. The phase transfer catalysis results in the transfer of ions from one phase to another phase in the vicinity of the phase transfer catalyst. The phase transfer catalyst is transferred not only anion but also cations, free radicals, whole molecules and even energy in chemical form (chemical form).

Advantages associated with PTC are:

- Reactions can be carried out in milder and safer conditions
- Reaction with very slow rate can be enhanced up to several extend
- Better yield and selectivity
- Reduction/elimination of solvent
- Reduces cost of chemicals
- Simplicity of process and equipment
- Simplified separation of products

1.9.1. History

In 1951, Jarrouse observed that biphasic reaction of benzyl chloride and cyclohexane and alkylation of phenylacetonitrile with benzyl chloride or ethyl chloride is accelerated by quarternary ammonium salt, i.e., benzyltriethylammonium. During the period 1950-1965, lots of research articles have been published on the use of quaternary ammonium or Phosphonium salts as PTC. Gibson, Hennis, Brandstrom, and Stark studied various reaction in which each of them was recognized by quaternary ammonium salts.

1.9.2. Mechanism of phase transfer catalysis

PTC involves a sequence of several steps, so in order to understand these steps influence of each step and their relationship need to be understood. Typical phase transfer catalyzed reaction involves following two steps:

I. Transfer of ion from its normal phase to into another phase
II. Reaction between the transferred ions and non-transferred reagent

According to the Stark's mechanism the PTC, dissolved in the aqueous phase (Q^+X) undergoes anion exchange reaction with the anion (Y^-), i.e., from aqueous phase reactant (RY) to form ion-pair (Q^+Y^-) which crosses the liquid-liquid interface as it is lipophilic in nature, then it diffuses from the interface into the organic phase (phase transfer step). Now in the organic phase, as the ion-pair is nucleophilic in nature, it undergoes a nucleophilic substitution reaction with the organic reagent (RX), forming the desired product (RY). Then the catalyst gets transferred back to the aqueous phase, and the cycle goes in the same way (Starks 1971).

1.9.3. Classification

On the basis of number of phases involved in the reaction, the phase transfer catalyst has been broadly divided into two categories

I. Biphasic PTC
II. Multiphasic PTC

Biphasic PTC can further be divided into liquid-liquid (L-L PTC) and solid-liquid PTC (S-L PTC) according to the actual phases involved in the reaction. The soluble phase transfer catalyst is inseparable in nature and hazardous to dispose directly to the environment. The

cost of the catalyst is pretty high, so the use of solid, reusable phase transfer catalyst is more recommended as phase transfer catalyst. Our investigation has emphasized on the use of a polymer-supported catalyst which is insoluble in nature hence, can be reused. These PTCs are multiphasic like liquid-liquid- solid (L-L-S), gas-liquid-solid (G-L-S), liquid-liquid-liquid (L-L-L), solid-liquid-solid (S-L-S), liquid-liquid-solid-liquid (L-L-S-L), etc.

1.9.3.1. Biphasic PTC

Liquid-Liquid (L-L PTC) and Solid-Liquid PTC (S-L PTC): In S-L PTC, nucleophile *($M^+ Y^-$)* is a solid dispersed in the organic phase. On the other hand, in the case of L-L PTC, it is dissolved in an aqueous phase (Maity et al. 2006). There are many applications of L-L PTC that have been reported, although the advantage in operating in the S-L mode is the elimination of the aqueous phase which decreases the degree of hydration of the ion pair and leads to an increase in its reactivity. The advantage of S-L PTC over L-L PTC is suppression of side reactions, increase in reactant surface area and mass transfer rate. In the case of L-L PTC, the reaction happens between the aqueous and organic phase, but in the case of S-L PTC, the reaction takes place between the anionic reagents and continuous organic phase.

1.9.3.2. Multiphase PTC

Solid (reagent)-liquid (ω)-liquid (org) PTC: In some S-L PTC, the limited formation of reactive ion pair on the surface of solid is encountered due to which the rate of reaction does not increase much, and poor regeneration of the catalyst is also encountered. So some trace of water is added to make the third phase, also known as ω phase, which helps to attain a high rate of reaction. In this phase, the crystal lattice is broken and becomes freely available for ion exchange and formation of quaternary ion pair. As the reaction proceeds, the S-L (ω)-L (org) turns to L (ω)-L (org) in which the nucleophile gets transferred to the organic phase for reaction with the substrate. This nucleophile accumulates in the ω phase. So, in this case, a limited amount of water leads to great enhancement of the rate of reaction, so no solvent is required. In the end, an excess of product or reactant is employed hence the waste is minimized (Yadav 2004).

Liquid-Liquid-Liquid PTC: When the solubility of catalyst in the organic and aqueous phase is limited, a third phase may result in the middle which is immiscible in both the phases. The stability of the third phase depends on various conditions like density difference, temperature and the phase equilibria of lipophilic and hydrophilic balance. In this mode of reaction, the reaction takes place in the third phase by transfer of both the liquid phase, i.e., aqueous and organic into the third phase. This mode of reaction has got

wide industrial acceptance. As the third phase, catalyst rich is immiscible in both the phases and therefore, it can be separated and reused. The aqueous phase can also be reused again. Hence, less amount of reagents are used, so waste is minimized (Yadav & Lande 2005; Yadav & Naik 2001).

Gas-Liquid-Solid PTC: G-L PTC is PTC in gas-liquid-solid systems, in which the phase of the organic substrate is gaseous and is passed over a bed of the inorganic reagent or some other solid reagent/co-catalyst. Advantages with the G-L PTC, it is easy to adapt continuous flow operation, no requirement of organic solvent, easy recovery of the catalyst as it is loaded directly into the bed of reagent and better selectivity than L-L PTC in some cases.

Liquid-Liquid-Solid PTC (Tri-phase catalysis): In this case of PTC, the catalyst is impregnated on the solid support and the support can either be polymer or inorganic which make it insoluble in the liquid phases. The catalyst like ammonium salts, phosphonium salts, macrocyclic polyethers, polar solvent residues and/or polyethylene glycols are impregnated on polymeric supports preferably polystyrene-based matrix cross-linked divinylbenzene (DVB). Contradicting to Stark's mechanism assumption (the catalyst moves freely in both the phases), in this mechanism, the movement of polymer-supported catalyst was stated to be confined in the interphase. Therefore, organic and aqueous phase need to be brought into contact with the catalyst in a sequential manner. The reaction takes place through the attachment and detachment of ions of aqueous and organic phase on the active sites of the catalyst that is better explained in the diagram of the reaction mechanism of TPC system (Fig.1.5).

The reaction occurs in different steps in which comprises of diffusion, attachment, detachment and again diffusion of ions (Satrio et al. 2000).

1. Nucleophile from the aqueous phase (HS^- and S^{2-}) travels from bulk to the vicinity of the inactive site of the catalyst through diffusion.
2. Attachment followed by Ion- exchange reaction between the nucleophile and the inactive site of the catalyst leaving the catalyst site active (Q^+HS^-) for further ion exchange. (The catalyst is marked as inactive when attached to its anion).
3. Diffusion of the organic substrate (RX) from bulk to the active site of the catalyst followed by ion exchange to form the product (RSH). During this ion exchange, the catalyst also gets regenerated to Q^+X^-.

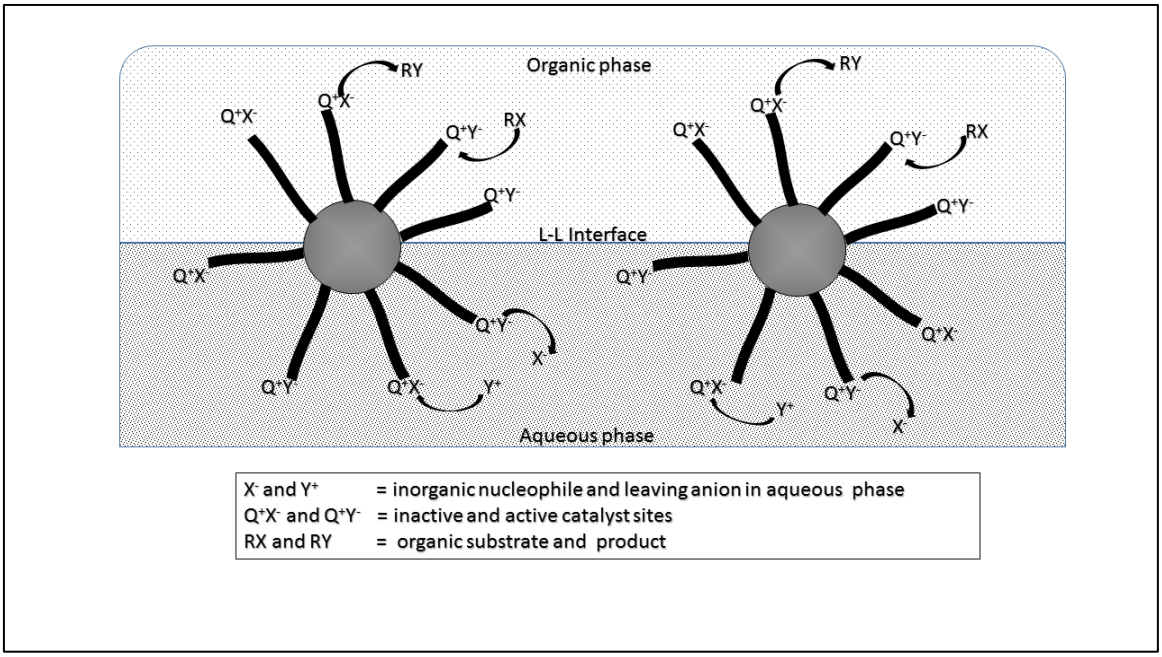


Fig. 1.5: The mechanism of L-L-S catalysis

1.10. Organization of the Thesis

The thesis is divided into several meaningful Chapters. The chapters included in the thesis are as follows:

Chapter 1: It gives the introduction to the topic, i.e., the problem associated with H_2S emission and various existing processes for H_2S capture and utilization.

Chapter 2: It comprises of background literature related to the topic of research.

Chapter 3: It consists of the materials and methods used for the work as well as the brief overview of the process of experiments and analysis.

Chapter 4: It encompasses on the detailed study of the kinetics, sensitivity, and mechanism for the synthesis of Bis-(p-chlorobenzyl) Sulfide in Liquid-Liquid-Solid PTC condition with using solvent toluene.

Chapter 5: It deals with the dual optimization of the responses, i.e., conversion of p-CBC and selectivity of BPCBS in the process of synthesis Bis-(p-chlorobenzyl) Sulfide using Response Surface Methodology.

Chapter 6: Detailed study of the kinetics and sensitivity for the synthesis of Bis-(p-chlorobenzyl) Sulfide under solvent free condition using Amberlite IR-400 as reusable PTC is described here.

Chapter 7: The chapter enlisted the conclusion of the present work and the future recommended.

CHAPTER 2

Background Literature

2.1 H_2S removal and utilization

Many scientists have patented the process of acid gas separation and absorption in absorbent (Tofik 2009). The natural gas contains hydrogen sulfide, carbon dioxide, and methane. For the removal of hydrogen sulfide selectively, dimethyl ethers of polyethylene glycol can be used under super-atmospheric pressure (Jameil and Seymour 1969). Natural gasses, coke-oven gasses, gasses from gasification of coal and synthesis gasses are washed using piperazine (0.81 to 0.13 moles/ liter) for removing impurities like H_2S, CO_2 and COS (Max et al. 1982). Hydrogen sulfide has been removed from the natural gas stream by contacting with a non-aqueous, water insoluble sorbing liquor which comprises of an organic solvent for elemental sulfur, dissolved elemental sulfur, an organic base to promote the reactions, and an agent suitable for maintaining the solubility of polysulfide intermediates (David 1998). In the study of H_2S and CO_2 removal from gaseous streams, Winkler used chelated Fe (III) for H_2S removal by converting it into elemental sulfur, and CO_2 was also removed to purify the stream gas (Winkler 1974). $FeBr_2$ has been used for the synthesis of Fe-EDTA catalyst complex which was further used as a catalyst along with iron chelated solution, for the purification of biogas. The process is carried out at room temperature and low pressure (Palma et al. 2013). Acid gasses can be extracted and regenerated using organic amines which are reactive with the acid gasses, and it can be regenerated by heating it to a higher temperature. If the dehydration of the gas is also required along with acid gas removal, then polyhydric alcohol is also added to the amine solution (Shapiro 1956). Aqueous ammonia solution has been used for H_2S absorption, and the H_2S laden aqueous ammonia was used as sulfiding agent for the synthesis of benzyl sulfide, an industrially valuable compound (Maity et al. 2006b). Study of sorption and desorption of H_2S on silica gel covered with a film of Triethanolamine (TEA) has also been studied (Zhou et al. 2004). H_2S absorbed in monoethanolamine (MEA) has been used as sulfiding agent for the synthesis of fine chemical dibenzyl sulfide (Sen et al. 2011). Diethanolamine (DEA) (Vallee et al. 1999), Diisopropanolamine (DIPA) (Yih and Sun 1987) and N-methyl diethanolamine (MDEA) are the alkanolamines which have been utilized for removal of H_2S by absorption and its utilization. Out of all other alkanol amines, MDEA has been found highly H_2S selective in the presence of other gasses like CO_2, so this has replaced all other Alkanolamines in the industries (Savage and Funkt 1986). The model based selective absorption of H_2S using MDEA has also been investigated (Bolhàr-Nordenkampf et al. 2004). The H_2S can be removed and utilized by desulfurization and absorption in aqueous ammonia followed by recovery of elemental sulfur. For desulfurization, H_2S has been treated with anthraquinone which is dissolved in the solvent having polarity higher than 5 Debye units, to produce elemental sulfur. The oxygen oxidizes the hydrocarbon fuel to produce hydrogen

gas used for the initial step of desulfurization (Plummer and Zimmerman 1986). Ammoniacal water stream followed by ammonia free water stream is used for H_2S removal and utilization. Ammonia free water was used to minimize the contamination of the gaseous stream with ammonia (Hamblin 1973).

Some researchers have changed their attention from amine solution to carbonate solution like aqueous K_2CO_3 (Faiz and Al-Marzouqi 2011). Water scrubbing (Lien et al. 2014) is also an economical process, as it uses very cheap and easily available solvent, i.e., water, that has been developed and being practiced in the different industries like biogas, natural gas, and petroleum refineries. Because of poor solubility and selectivity towards H_2S, water scrubbing process is not recommendable for a high level of H_2S removal. Sulfoxo is one of the industrially adopted processes of removal and utilization of H_2S (Srivastava and Singh 2014). There are some microbiological or biological processes available for H_2S removal. For the bio-oxidation of H_2S, phototropic as well as chemotropic bacteria is used. Phototropic *C. limicola* is ideal bacteria for the process due to its ability to grow under anaerobic condition using an only inorganic substrate (Syed et al. 2006). Bio-Sulfex biofilters of ATZ-EVUS is used for H_2S removal from biogas by biological desulfurization method (Schieder et al. 2003). The level of H_2S can be minimized or removed using a hybrid process (membrane separation and absorption in DEA), bio filtration and ZnO nanoparticles at a lower temperature. In the hybrid process of removal of acid gas, 40% of CO_2 and 1% of hydrogen sulfide was removed, firstly, for bulk removal of the acid gases, membrane separation method was used whereas for the final separation was achieved by gas absorption using diethanolamine (Bhide et al. 1998). Biofilters are also being used for control of the level of H_2S in the waste gas. The biofiltration method utilizes microorganisms which are immobilized on a porous filter substrate and forms a film over it (Yang and Allen 1994). The well-ordered, hydrothermally stable mesoporous molecular silica SBA-15, supported on ZnO nanoparticles can also be used for H2S removal at low temperature (298 K). For the method, mesoporous molecular silica SBA- 15, supported on ZnO was prepared by incipient wetness impregnation and ultrasonic method along with in situ activation at 523 K (Wang et al. 2008).

2.2. Dibenzyl sulfide and bis-(p-chlorobenzyl) sulfide

Thioethers like bis-(p-chlorobenzyl) sulfide (BPCBS) and dibenzyl sulfide (DBS) are out of those fine chemicals which are being synthesized using H_2S laden amines or other processes too as they have found their applications as anti-wear additives for motor oils,

additives for extreme pressure lubricants, in different anticorrosive formulation, stabilizers for photographic emulsions and refining and recovery of precious metals (Pradhan and Sharma 1992). Some useful synthetic intermediates like dibenzyl sulfoxide and dibenzyl sulfone formulations can be synthesized by oxidation of DBS. This sulfoxides and sulfones are industrially important as it has a wide range of application in biological and pharmaceuticals industries. For this ammonium cerium (IV) nitrate and KBr or NaBr used as a catalyst in the presence of wet silicon oxide in CH_2Cl_2 (Zolfigol et al. 2008).

Synthesis of DBS and BPCBS has been done in Liquid-Liquid (L-L) and Solid-Liquid (S-L) PTC mode of reaction using sodium sulfide and p-chlorobenzyl chloride (p-CBC) & benzyl chloride respectively. The first detailed kinetic study was firstly presented by the Pradhan and Sharma; they used tetrabutylammonium bromide as phase transfer catalyst under L-L and S-L conditions. In the same work, they studied the effect of Ω phase on the S-L mode of reaction by addition of a little amount of water (Pradhan and Sharma 1990). Study of the kinetics of synthesis of DBS using solid sodium sulfide in S-L PTC in the presence of a solid catalyst, basic alumina, and Amberlyst A27 (Cl^- form) anion exchange resin has been well documented. In this study, alumina was used as a cocatalyst with tetrabutylammonium bromide for the S-L mode of reaction between benzyl chloride/p-chlorobenzyl chloride with sodium sulfide (Pradhan and Sharma 1992). DBS has been synthesized from benzyl chloride using tetrahexylammonium bromide as phase transfer catalyst (PTC) (Maity et al. 2006b). DBS has been synthesized by reducing corresponding disulfides in the presence of Zn powder using $AlCl_3$ aqueous media (Lakouraj et al. 2002). Reduction of sulfoxide using Al-$NiCl_2$-$6H_2O$ as reducing agents was also performed for the synthesis of DBS (Raju et al. 2004). Because of expensive reagents, long reaction time and extreme reaction conditions, the reduction was not found to be an economical method (Iranpoor et al. 2002).

2.3. Phase transfer catalyst

Phase transfer catalysis is a mature technique of intensifying biphasic reactions. Many researchers have been indulged in the field of phase transfer catalysis for years. Thousands of literature are available in this field. In 1971, Starks had developed the first mechanism and gave the name to the catalyst as “phase transfer catalyst” (Starks et al. 1971). Later on, Napier and Starks have patented their research on heterogeneous catalysis using quaternary salts (Napier and Starks 1976). There are various types of modes of reactions in case of phase transfer catalyst like L-L, L-L-L, L-L-S, L-S, etc., depending on the various work already

performed. Pradhan and Sharma have used Tetrabutylammonium bromide (TBAB) as phase transfer catalyst for the S-L mode of reaction besides they have also studied the effect of Ω phase on the reaction kinetics (Pradhan and Sharma 1990). The same group of researchers has studied the effect of co-catalyst and ultrasound on the rate of the same reaction (Pradhan and Sharma 1992). The L-L mode of phase transfer catalyzed reaction can be carried out for the separation of phenol aqueous alkaline media by its reaction with allyl bromide dissolved in dichloromethane (Liu and Road 1998). L-L-L mode of catalyst or development of third phase has always been an attractive technique of enhancing in rate of reaction in the multiphase reaction system (Baj and Siewniak 2010; Baj and Siewniak 2007; Baj et al. 2012; Hsiao and Weng 2013; Yadav and Badure 2009; Yadav and Badure 2008; Yadav and Motirale 2010; Yadav and Sowbna 2012; Yang and Chen 2009; Yang and Huang 2011; Yang and Lin 2011). The fine chemicals like p-nitroanisole and p-nitrophenitole were synthesized by p-nitrobenzene, sodium hydroxide with methanol or ethanol in the presence of tetrabutylemethylammonium bromide under L-L-L mode of reaction (Yadav and Naik 2001). For the synthesis of dibenzyl ether from benzyl chloride and benzyl alcohol, dodecane and tetraalkylammonium bromide were used for development of the third liquid phase (Jin et al. 2003). A brief discussion on the types, activity, conditions for the third phase, and reuse of the catalyst has been documented by Goto (Goto 2004). The synthesis of allyl phenyl ether by esterification of allyl bromide and sodium phenolate with tetra-n-butylammonium bromide (TBAB) as PTC was studied. Besides this, the study of the effect of the addition of small amount of Na_2CO_3 on the conversion of the reactant and yield of the product was also studied (Hsiao and Weng 2004). The formation of the third liquid phase in the reaction has been studied where tetrabutylammonium bromide or polyethylene glycol or both were used for development of the third phase with n-butanol and potassium hydroxide (Jin et al. 2004). TBAB was again used for the third liquid phase catalyzed the esterification of sodium o-nitrophenoxide and 1-bromooctane to form o-nitrophenyl octyl ether (Lin and Yang 2005). The kinetics of the synthesis of 4-acetylphenyl benzoate from benzoylation of sodium 4-acetylphenoxide was studied, and the kinetics was found to be dependent on the intensity of agitation (Huang and Yang 2005). The esterification of vanillin with benzyl chloride under L-L-L phase transfer catalysis to produce a compound that has got an application in perfumery industry was achieved along with that the effect of the different parameter on the synthesis was also studied (Yadav and Lande 2005). The esterification of sodium salicylate with benzyl bromide was carried out under L-L-L mode of catalysis (Yang and Li 2006).

There are many review articles present which describes different aspects of PTC (Fiamegos et al. 2006). The different properties of PTC like solubility, surface chemistry, mass

transfer, distribution in both the phases, ion pair equilibria has been very well written by Jwo. On the other hand, the document contains a brief idea of the different types of a catalyst based on its solubility in different solvents and different types of bond in the molecule catalyst (Jwo 2003). In other review articles also the kinetics, ion solubility, and anion activation like properties have been discussed (Gokel and Weber 1971). Benaglia in his article "polymer supported organic catalysts" has described the different types and structure of the supported phase transfer catalysts (Benaglia et al. 2003). A very well written article describing the different process of intensifying the rate of multiphase reactions and the classification of PTC based on the number of phases is also available (Yadav 2004). Naik and Doraiswamy have documented the classification of PTC based on their solubility, and they also described the models and mechanism of different PTCs (Naik and Doraiswamy 1998). The soluble PTC has been successfully used in various literature. For the synthesis of dibenzyl sulfide sodium sulfide with benzyl chloride was used in the presence of tetrahexylammonium bromide as PTC. The operation was carried out in L-L mode of catalysis (Ido et al. 2000). Maity has worked in the area of PTC and has used TBAB as PTC for reduction of nitrochlororbenzene and synthesis of Dibenzyl sulfide (Maity et al. 2006c; Maity et al. 2006a; Maity et al. 2009). Monoethanolamine (MEA) was used for H_2S capture, and then the aqueous H_2S rich MEA was used as sulfiding agent for Synthesis of Dibenzyl Sulfide (Sen et al. 2011). The synthesis of benzaldehyde by oxidation of benzyl chloride is also a biphasic reaction that can be intensified by the use of H_2O_2 as phase transfer catalyst (Yadav and Mistry 1995). Use of microwave irradiation to intensify the rate of reaction has also been done (Yadav and Bisht 2004). The phase transfer catalysis has been used for reduction nitroanisole to p-anisidine (Yadav et al. 2003). P-chlorophenyl acetonitrile has been synthesized by TBAB as PTC and KOH as co-catalyst. Hence, the role co-catalyst, for intensifying rate of reaction, has been studied (Yadav and Jadhav 2003). There are many other kinds of literature available where soluble PTC has been used (Yang and Lin 2003; Yang and Huang 2006; Zhao et al. 2007).

Copious literature has been found in the use of triphase catalysis (L-L-S), as the catalyst can be reused, the catalyst has been recognized for green synthesis (Sun et al. 2009; Movassagh and Rezaei 2014; Jadhav et al. 2012). As the mass transfer effect plays an important role in solid PTC for measurement of the coefficient of mass transfer catalyst a new rotating disk contactor was introduced and operated (Glatzer et al. 1998). As the solid catalyst is immobilized PTC, mass transfer effect plays a major role in triphase catalysis so the mass transfer role can't be neglected and for the modeling of the triphase catalytic system, we need to have a good idea of the effect of mass transfer and its correlation. From previous literature, it has been found that mass transfer is dependent on the agitation speed. For the calculation of

mass transfer coefficient, a correlation among Sherwood number to the Reynolds and Schmidt numbers has been proposed (Glatzer and Doraiswamy 2001). The polymer-supported catalyst molybdenum carbonyl catalyst has been synthesized by immobilizing Molybdenum hexacarbonyl on polystyrene. Alkenes with tertbutyl hydroperoxide have been converted to epoxides using the synthesized catalyst with good yield. The synthesized triphase catalyst has been found to be highly reusable (Grivani et al. 2005). $Mo(CO)_6$, immobilized by polystyrene two can also be used for epoxidation of alkenes that is used as a heterogenous catalyst in the presence of *tert*-butylhydroperoxide. Polymer bound shift legand was prepared by oxidation of chloromethylated polystyrene to aldehydic polystyrene 1 and then reaction with ethylene diamine (Grivani et al. 2007).

The comparison of different polymer supported PTC for the industrial synthesis of bisphenol-A from phenol and acetone has been documented (Yadav and Kirthivasan 1997). The mechanism and kinetics of the selective synthesis of benzaldehyde from benzyl chloride using polymer supported chromium salt as PTC have been studied (Yadav and Haldavanekar 1997). Satrio has described the activity and mechanism of the polymer-supported catalyst as well as he has developed a general kinetic model (Satrio et al. 2000). A soluble polymer bound catalyst can also be synthesized which can be recovered by exploiting their characteristic solubility in a limited solvent in the specific temperature range (Grinberg and Kas 1997).

CHAPTER 3

Experimental

3. Material and methods

3.1. Materials

Toluene (>99%), N-methyl diethanolamine (MDEA) (>99%) and p-chlorobenzyl chloride (p-CBC) (>99%), all of the analytical reagent grade, were procured from Sigma-Aldrich, Mumbai, India. The catalyst polymer-bound tributylmethylphosphonium chloride was purchased from Sigma-Aldrich, Mumbai, India. The FeS sticks used for H_2S production has been bought from Rankem, India. Amberlite IR-400 has been procured from Ranken. Potassium iodide (KI), Sodium hydroxide (NaOH), potassium iodate (KIO_3), starch powder, sodium thiosulfate ($Na_2S_2O_3$) and 98% pure sulfuric acid (H_2SO_4) have been bought from Renken for absorption of H_2S and determination of sulfide concentration.

3.2. Preparation of aqueous of H_2S-rich N-methyldiethanolamine

H_2S gas, produced in the Kipps Apparatus by reaction of FeS sticks with dilute Sulfuric acid (Eq. 3.1) was passed through aqueous N-methyldiethanolamine (MDEA) solution, kept in an ice bath to prevent oxidation sulfides. The concentration of sulfide was estimated using iodometric titration method.

$$FeS + H_2SO_4 \rightarrow H_2S + FeSO_4 \quad (3.1)$$

3.3. Measurement of sulfide concentration (Iodometric titration)

1. From the stock solution of H_2S laden MDEA, 1 ml of the solution was taken out then it was diluted to 100 times with distilled water. 10 ml of the diluted sulfide solution was taken is a conical flask, and 15 ml of 0.025 M KIO_3 solution was added followed by addition of 10 ml of 10 M NaOH solution.
2. The mixture was boiled for 10 min, cooled under tap water and kept in the refrigerator.
3. 5 ml of 5% KI solution was then added to the mixture followed by 20 ml of 4 M H_2SO_4 solution. (the mixture color turned to brown)
4. The solution was titrated against 0.1 M thiosulfate solution till the color of solution changes to pale yellow.

5. The solution was then diluted up to 200 ml using distilled water, and a few drops of 0.2% starch solution were added. (the colour changes to violet)
6. The solution was again titrated against the thiosulfate solution dropwise till the solution becomes colourless.

The reactions involved in the process are as given below, Eq. (3.2) – (3.3):

$$KIO_3 + H_2SO_4 + 5KI = 3K_2SO_4 + 3I_2 + 3H_2O \quad (3.2)$$

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI \quad (3.3)$$

$$4IO_3^- + 6OH^- + S^{2-} = 4SO_4^{2-} + 4I^- + 6H_2O \quad (3.4)$$

Thus, the 1 mole of KIO_3 = 3×2 moles $Na_2S_2O_3$,

$$\therefore \text{Strenth of Thiosulfate Solution } (S_{th}) = \frac{6 \times \text{Strenth } (KIO_3) \times \text{Volume } (KIO_3)}{\text{Volume (Consumed Thiosulfate)}}$$

Here**,** the volume of thiosulfate consumed in the titration is for the first titration.

And, 4 moles of liberated iodine $(IO_3^-) = 3$ moles of sulfide (S^{2-}) (for the second titration)

$$\text{so, the Concentration of } H_2S = \left[15 \times S_{KIO_3} - \frac{V_{th} X S_{th}}{6}\right] \times \frac{3}{4} \times \frac{N_{dl}}{10}$$

Where,

V_{th} = Thiosulfate volume

N_{dl} = Number of times of dilution

S_{KIO_3} = KIO_3 Strength

S_{th} = Thiosulfate Strength

3.4. Experimental set-up

All the experiments were performed in a fully baffled three-neck flask with a stirrer. The typical dimensions of the apparatus were 150 cm^3 volume of the flask, where all the

experiments were carried out, and the stirrer has a blade diameter of 2 cm with six blades. The whole apparatus was assembled in an isothermal water bath with PID temperature controller to provide uniform heating to the reaction, and direct-drive digital stirrer was installed with the stirrer to provide constant stirring of the reaction. The whole reaction set-up is as shown in the Fig. 3.1.

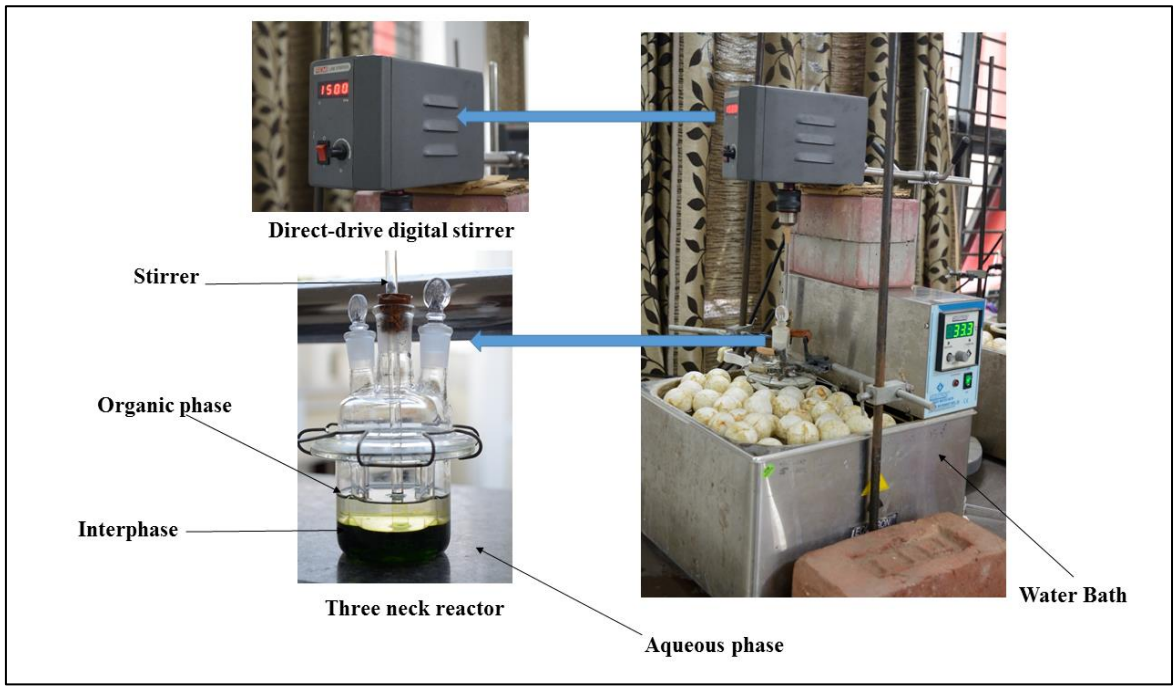


Fig. 3.1. The Experimental Assembly

3.5. Experimental methods

Two approaches were adopted to carry out the reaction and then analysis of the results – conventional one-variable-at-a-time approach to carry out the kinetic experiments and Statistical Design of Experiment (DoE)

3.5.1. One variable at a time approach

The method of changing one variable at a time (OVAT) (Ref chapter 5) has been used for the kinetic study of the synthesis of bis-(p-chlorobenzyl) sulfide under L-L-S condition using tributylmethylammonium chloride polymer bound with toluene as solvent and Amberlite IR-400 under solvent free condition.

3.5.2. Design of experiments (DoE)

We have used the design of experiments for the dual optimization of conversion of the reactant p-CBC and selectivity of the product BPCBS. RSM with Central composite design CCD which is the most popular class of second order design has been used for this investigation. Using this model, we have studied the effect of different parameters that alter the conversion of p-CBC and selectivity of the BPCBS. Optimization of different parameters for maximizing conversion and selectivity has also been successfully employed.

We have used RSM with five level four-factor CCD. The range of the values for different parameters taken for the experiment design is tabulated in Table 5.1. The range chosen for the work is based on literature on the related area of research, result in the previous experiment, reaction set up, availability and cost of different reagents. For statistical calculations, the variables X_i were coded as x_i according to the following relationship:

$$x_i = \frac{X_i - X_0}{\Delta X} \tag{3.5}$$

Minitab (version 16.1.1), Hewlett-Packard Co. has been used for main plot and the statistical software package Design-Expert (version 8.0.2), Stat-Ease, Inc., Minneapolis, USA, has been used for multiple regression analysis of experimental data to fit the polynomial equations. Using the mentioned software, development of 3D response surfaces and contour plots was achieved. This has been done by using the fitted polynomial equation obtained from the regression analysis. For this two of the independent variables are kept constant value corresponding to the stationary point, and the other two variables are changed. The fitting quality of the model has been examined by the coefficient of determination (R^2 and adjusted R^2) and analysis of variance (ANOVA). Statistical parameters have been estimated using ANOVA. Some insignificant coefficients have been manually removed after evaluation.

Multi-response optimization using Desirability Function

Desirability function approach has widely been adopted as a method to optimize multiple response processes. It signifies the quality of the process that has multiple quality characteristics in which if one of the characteristics is out of the desired limit, the process is entirely unacceptable. Let for a particular process condition x provides the most desirable condition. $Y_i(x)$ represents the response at x condition with desirability function $d_i\ (Y_i)$ (where $0 \leq d_i\ (Y_i) \leq 1$) when $d_i\ (Y_i) = 0$ represent completely undesirable value and

$d_i\ (Y_i)$ = 1 represents ideal response. The geometric mean of individual desirabilities is given by overall desirability function D for K no of response, as shown in the equation (3.6).

$$D = \left((d_1\ (Y_1)).(d_2\ (Y_2)\right) \ldots\ldots (d_K\ (Y_K)))^{1/K} \quad (3.6)$$

The value of d_i increases as the "desirability" of the corresponding response increases. The optimization module in Design Expert searches for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. The possible objectives: maximize, minimize, target, within range, none (for response only) and set to an exact value (factors only).

3.6. Experimental procedure

Firstly, we charge the measured quantity of catalyst to the reactor, followed by required of aqueous sulfide solution (H_2S laden MDEA) of known concentration. The organic phase (p-chlorobenzyl chloride), either with or without solvent was then poured into the batch reactor, and when the temperature of the water bath reaches its set point, the stirrer was turned on at a certain rpm to start the reaction. The samples were collected after specified time interval using micropipette from organic phase after turning the stirrer off and allowing the phases to separate and bubbles of the discontinuous phase to coalesce to stop the reaction between the phases.

3.7. Analysis of the phases

In the present investigation, quantitative analysis was done using GC-FID (Agilent GC 7890B) equipped with a capillary column (DB-5MS, 2m × 3mm) using a flame ionization detector. The qualitative analysis/product identification was done using GC-MS (Agilent 5977A).

3.7.1 Qualitative analysis using GC-MS

A known volume of organic sample was injected into the column using a micro syringe which was carried with the carrier gas helium. The compounds present were identified by GC-MS. For the separation molecules (present in the sample), a capillary column is used in the GC-MS. In the column the sample goes to the mass spectrometer capture, then it ionizes, accelerates, deflects and the molecules are finally detected

separately. The different molecular weight of the different compound is given in the spectra, and BPCBS was identified as molecular weight 283. A detailed program followed for the identification in GCMS is given below:

MS Program

Inlet conditions. (Split mode)

Purge Flow = 3 ml/min, Heater = 300^0C, Pressure = 11.724 psi

Column specifications. Agilent DB-5ms, Flow = 1 ml/min, Pressure = 8.2317 psi, Holdup Time = 1.365 min

Oven condition. Initial Temperature = 60 ^{0}C, Maximum temperature = 300 ^{0}C.

Table 3.1 Temperature Programme for MS

	Rate (^{0}C/min)	**Value (^{0}C)**	**Holdup Time (min)**	**Retention Time (min)**
Initial		60	0.25	0.25
Ramp 1	100	150	0.00	1.15
Ramp 2	50	300	5.00	9.15

3.7.2 Quantitative analysis using GC-FID

Gas-chromatography accompanied with flame ionization detector (GC-FID) is being widely used natural gas, petroleum, and pharmaceutical markets. For the analysis, we inject a known volume of the sample using microsyringe into the capillary column. In the present analysis, nitrogen acts as a carrier gas which carries the molecules of the sample through the column, and the molecules get adsorbed in the fillings present in the column which is the stationary phase of the column. Every molecule differs in their progression rate and leaves the column at a different time which is called the retention time of that molecule. The molecules which are leaving the column is detected by a flame ionization detector. The sample passes through a Hydrogen/Air flame to oxidize organic molecules and produces electrically charged ions. These ions get collected and generate an electrical

signal which is then measured. The concentration of the organic compound is proportional to the number of ions formed, and this theory was used quantification of the organic phase. The detailed program followed for the quantification using GC-FID is mentioned below:

FID Program

Inlet Condition. Heater = 200 ^{0}C, Purge Flow = 3ml/min, Pressure = 15.345 psi

Column Condition. Agilent DB-5ms, Flow = 1.5 ml/min, Holdup Time = 1.427 min, Pressure = 15.345 psi.

Oven Condition. Initial temperature = 60 ^{0}C, Maximum temperature = 300 ^{0}C.

Detector. Heater = 300 ^{0}C, Column Flow (N_2) = 15 ml/min, Make up Flow (N_2) = 25 ml/min, H_2 Flow = 30 ml/min, Air Flow = 400 ml/min.

Table 3.2 Temperature Programme for FID

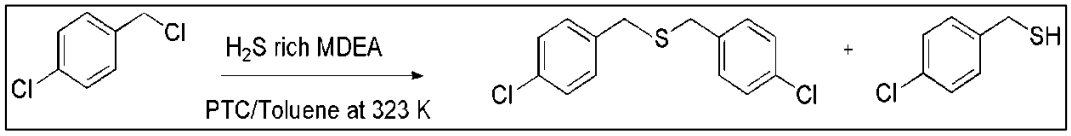
	Rate (^{0}C/min)	**Value (^{0}C)**	**Holdup Time (min)**	**Retention Time (min)**
Initial		50	0.0	0.0
Ramp 1	30	170	0.0	4.0
Ramp 2	50	260	0.0	5.8
Ramp 3	10	280	4.2	12

CHAPTER 4

Kinetic Studies in Synthesis of Bis-(p-chlorobenzyl) Sulfide

4.1. Introduction

Commercially H_2S is captured efficiently using alkanolamines such as methyldiethanolamine (MDEA). Aqueous H_2S-rich MDEA is proposed to act as a sulfiding agent for aromatic halides such as p-chlorobenzyl chloride (p-CBC) to synthesize value-added thioethers. The objective of the present investigation is a selective synthesis of a value-added thioether - bis-(p-chlorobenzyl) sulfide (BPCBS) using p-CBC and H_2S-rich aqueous MDEA. For the immiscible bi-phasic system, reusable solid phase transfer catalysts polymer bound tributylmethylammonium chloride (PBTBMAC), tributylmethylphosphonium chloride (PBTBMPC) and Amberlite IR-400 were employed under the liquid-liquid-solid (L-L-S) mode of reaction in the presence of solvent toluene to enhance the reaction rate and product selectivity. The products were identified by the gas-liquid chromatography (GLC). The overall stoichiometric Eq. of the reaction between p-CBC and H_2S laden MDEA is as shown below in the Eq. (4.1).



(4.1)

The sensitivity analysis of the reaction with respect to different reaction conditions like temperature, catalyst, reactant, sulfide, and MDEA concentration was performed. We also compared the catalyst with other catalysts. The catalyst has shown substantial activity even after three times of reuse. This leads to waste minimization and economic benefits. A generalized empirical kinetic model was developed and successfully validated against the experimental results.

4.2. Result and discussion

4.2.1. Proposed mechanism

In this investigation, polystyrene supported tributylmethylammonium chloride catalyst has been used which can be regenerated using NaCl solution. H_2S is absorbed in the MDEA solution and with the known concentration of sulfide in this aqueous phase and p-CBC are reacted.

The whole mechanism of L-L-S was found to be very complex. The reaction between H_2S, MDEA and H_2O forms ionic complexes like RNH^+HS^-, $(RNH)_2S$ that reacts with the organic reactant p-CBC to form p- CBM as shown in the Eq. (4.13) (Scheme 4.1) or form final product BPCBS. The intermediate p- CBM combines with the excess organic reactant p-CBC to form final product BPCBS as shown in stoichiometric Eq. (4.14).

4.2.2. Reaction in aqueous phase

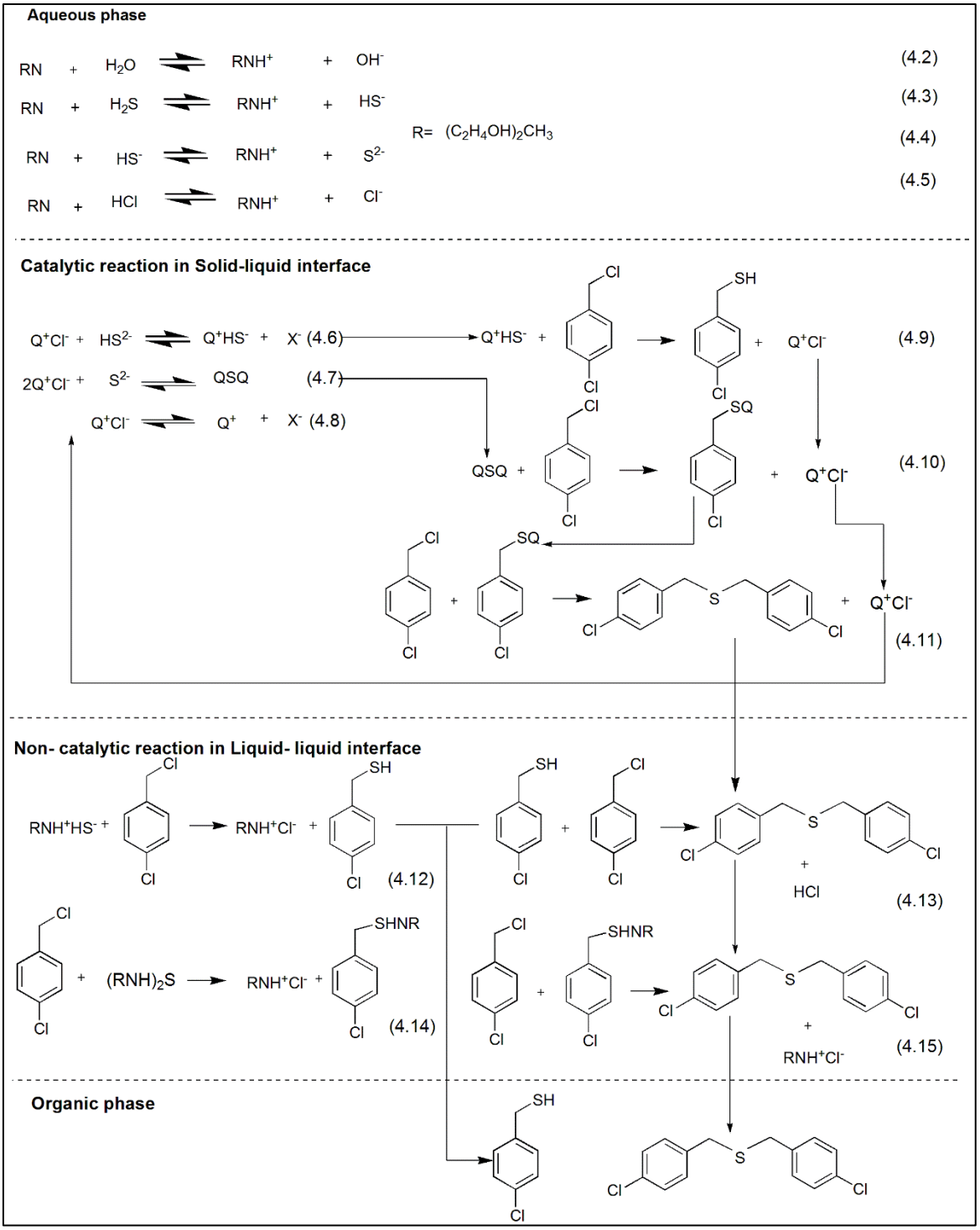
The aqueous phase contains, MDEA and H_2S absorbed in it. The reaction among H_2S, MDEA and H_2O forms ions like HS^-, S^{2-} and OH^- as shown in the Eq. (4.3), (4.4), (4.5) and (4.6) (Singh et al. 2016). These nucleophiles migrate from bulk of the aqueous phase to the catalytic interface, then attachment of nucleophile occurs at the inactive site of the catalyst followed by the ion exchange reaction as shown in the reaction Eq. (4.7)- (4.9). This ion exchange reaction is very fast and always considered to be in equilibrium.

4.2.3. Non-catalytic contribution

The presence of the solvent and the rigorous stirring of both phases trigger the rate of the reaction. The reaction between the organic and inorganic phase in the absence of the catalyst is also found to be enough to be taken into the consideration (Scheme 4.1). These ionic complex RNH^+HS^- reacts with the organic reactant p-CBC to form p- CBM as shown in the Eq. (4.13), which can again react to the organic reactant p-CBC to form the final product BPCBS. The S^{2-} plays a major role in the synthesis of product BPCBS as it forms the complex $(RNH)_2S$ with MDEA that combines with two molecules of p-CBC to form BPCBS. This reaction is a two steps process as shown in the Eq. (4.15) and (4.16). The products p- CBM and BPCBS diffuse back to the organic phase when reaction stops.

4.2.4. Catalytic contribution

These nucleophilic ions migrate from bulk of the aqueous phase to the catalytic interface where attachment of nucleophile to the inactive site of the catalyst occurs, followed by the ion exchange reaction as shown in the reaction Eq. (4.7)- (4.9). This ion exchange reaction is very fast and so always considered to be in equilibrium. As the active sites are immobilized on the catalyst itself, so reactants sequentially come in the contact of the catalyst, as shown in the Eq. (4.10)-(4.12). The reactant, p-CBC travels to the active site and ion exchange takes place in between to form p-CBM and BPCBS. The whole mechanism is shown in Scheme 4.1.



Scheme 4.1: The proposed mechanism for synthesis of BPCBS L-L-S reaction

4.3. Sensitivity study

4.3.1. Effect of catalyst concentration

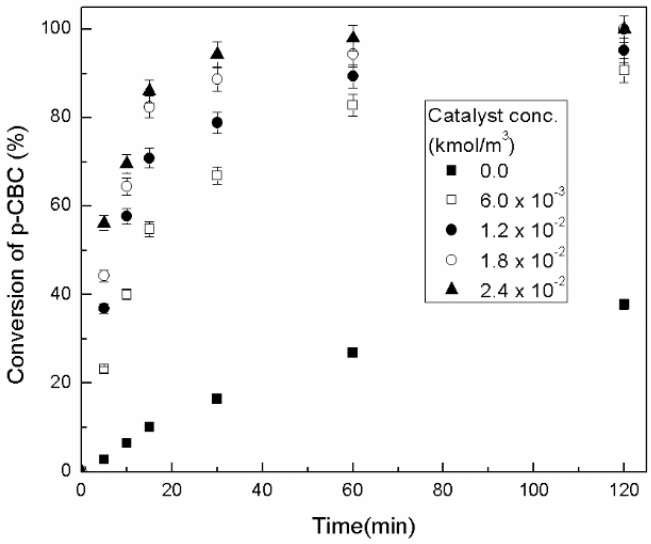
The catalyst concentration was varied from 0 to 2.4×10^{-2} kmol/m^3 and its effect on p-CBC conversion, and BPCBS selectivity was plotted against time as shown in Fig.4.1 (a) and (b). The selectivity of BPCBS and conversion of p-CBC were found to be 30% and 40% respectively without catalyst and both of them shoots up to 100% for the catalyst concentration of 2.4×10^{-2} kmol/m^3. The S^{2-} and HS^- ions form catalyst active intermediates QSQ and QSH that combines with p-CBC to form BPCBS and p-CBM. Upon increasing catalyst concentration, the concentration of these intermediate increases and hence the conversion of p-CBC and selectivity of BPCBS also increases (Sen et al. 2011). The enhancement of reaction rate with catalytic loading can also be observed in terms of enhancement factor as shown in Table 4.1. For minimizing the catalyst consumption for each run, the optimum catalytic concentration was chosen as 6.0×10^{-3} kmol/m^3 for rest of the reactions.

Table 4.1

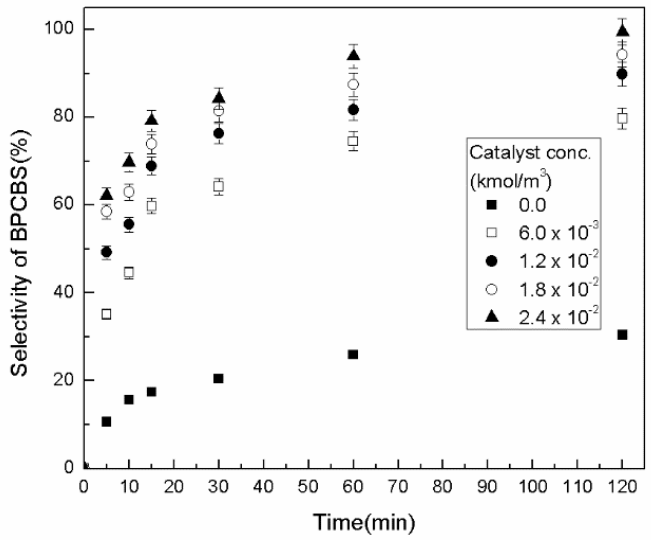
Effect of catalyst loading on initial rate of reaction and enhancement factor [a]

Catalyst Loading × 10^5 (kmol/m^3)	**Initial Rate of Reaction × 10^3 (kmol/m^3.s)**	**Enhancement Factor**
0.0	0.217	1.0
0.6	3.135	14.4
1.2	3.700	17.1
1.8	4.638	21.4
2.4	5.200	24.0

[a] All other conditions are same as Fig. 4.1.



(a)



(b)

Fig. 4.1. The effect of catalyst concentration on (a) conversion of p-CBC and (b) selectivity of BPCBS.

Thermochemical condition: Volume of aqueous and organic phase 2.5×10^{-5} m^3 each, temperature: 323 K, MDEA concentration: 3.0 kmol/m^3, stirring speed- 1500 rpm, reactant concentration: 2.4 kmol/m^3, sulfide concentration of aqueous phase: 2.0 kmol/m^3.

The order of the reaction with respect to the catalyst concentration was calculated by a plotting graph between ln (initial rate) and ln (catalyst concentration). The slope of the graph was found to be 0.63 from Fig.4.2, is the order of the reaction with respect to catalyst concentration.

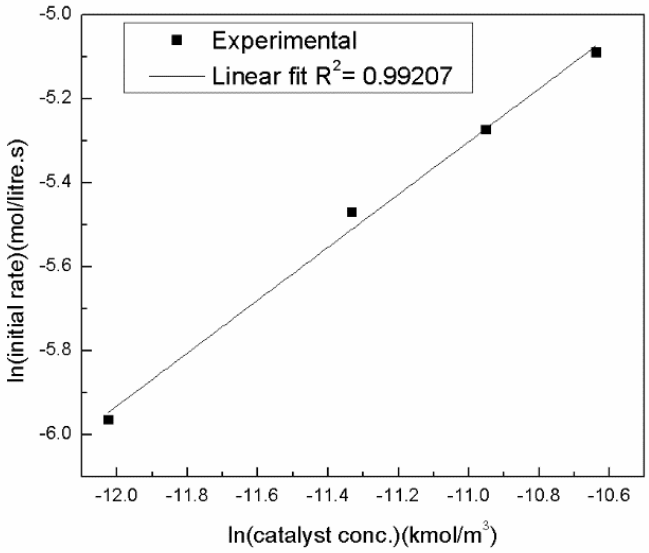


Fig. 4.2. Plot between ln (initial rate) and ln (catalyst conc.) (All conditions are same as mentioned under Fig. 4.1.)

4.3.2. Comparison with different catalysts

For the establishment of the superiority of the catalytic activity the catalyst, polymer-bound tributylmethylammonium chloride (PBTBMAC) over other catalysts, insoluble PTC like Amberlite IR-400 and soluble PTC like Tetrabutylphosphonium bromide (TBPB) and Ethyltriphenylphosphonium bromide (ETPB) were chosen. All catalysts were used at same concentration i.e. 6.0×10^{-3} kmol/m^3 keeping all the parameters at optimized values. The best result was observed in the case of PBTBMAC (Fig. 4.3). From past literature we have found that the activity of the polymer-supported catalyst is greater than the soluble catalyst due to reasons like increase in its lipophilicity due to its polymer backbone, the microphase effect of catalyst, and substrate selectivity (Desikan and Doraiswamy 2000; Satrio et al. 2000). For both the soluble catalysts, their distribution in both the phases is necessary for which again more amount of catalyst is required. But polymer-supported catalyst PBTBMAC doesn't get distributed in both of the phases; its active sites are responsible for the reaction that gets activated and deactivated time and again throughout the reaction. So, it is effective at very low concentration. Thus, the results

imply that the catalyst PBTBMAC is not only reusable but also gives a very good conversion of the reactant at remarkably low concentration.

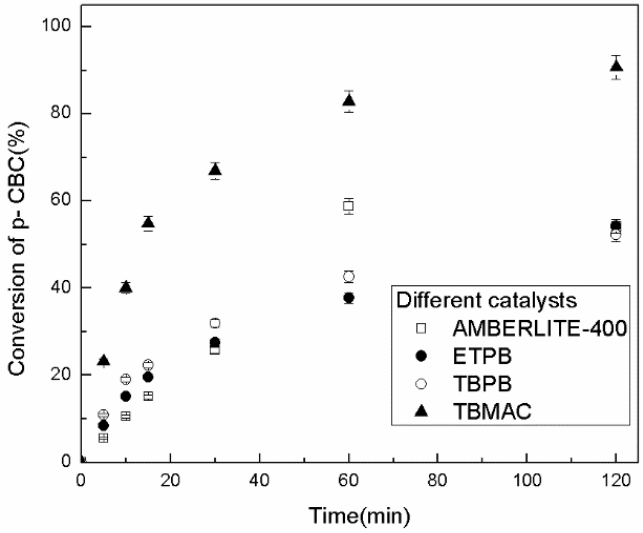
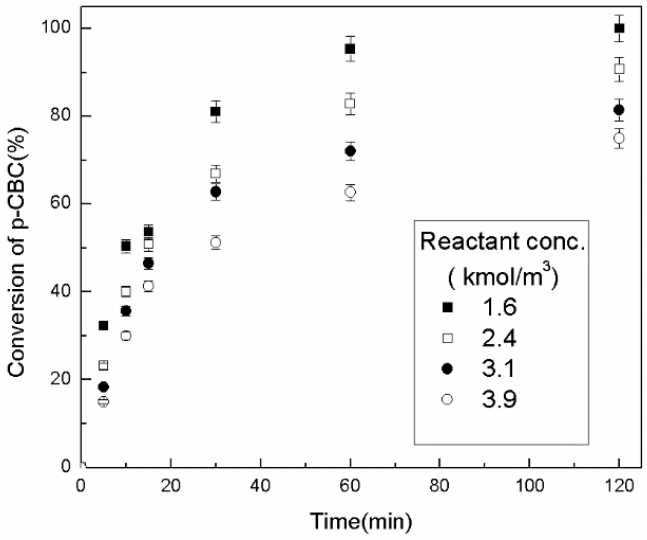


Fig. 4.3. Effect of the different catalysts on conversion of p-CBC

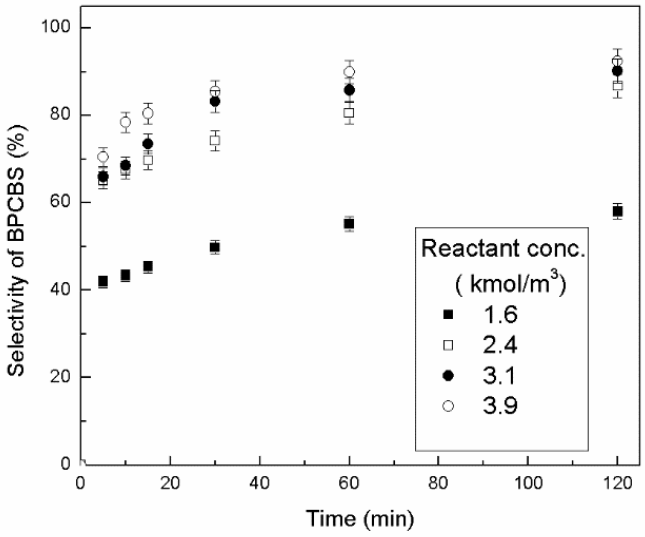
Thermochemical condition: Volume of aqueous and organic phase: 2.5×10^{-5} m^3 each, MDEA concentration: 3.0 kmol/m^3, temperature: 323 K, Stirring speed- 1500 rpm, all catalyst concentration: 6.0×10^{-3} kmol/m^3, reactant concentration: 2.4 kmol/m^3.sulfide concentration: 2.0 kmol/m^3.

4.3.3. Effect of reactant concentration

The effect of reactant concentration on conversion of p-CBC and selectivity of BPCBS was observed by varying the p-CBC concentration from 1.6 to 3.9 kmol/m^3 as shown in Fig. 4.4. It is clearly visible from Fig.4.4. (a), that conversion of p-CBC decreases with increase in p-CBC concentration. Decrease in consumption of the reactant p-CBC with more p-CBC is due to the presence of a limited amount of S^{2-} and HS^- ions in the aqueous phase. On the other hand, the selectivity of BPCBS increases with increasing reactant concentration as the undesired product i.e. PCBM, recombines with the excess unreacted p-CBC to form more BPCBS (Fig.4.4. (b)). For simultaneous optimization of conversion of reactant along with the selectivity of the product, an average value of p-CBC concentration i.e. 2.4 kmol/m^3 was taken for all other reactions.



(a)



(b)

Fig. 4.4. The effect of reactant concentration on (a) conversion of p-CBC and (b) selectivity of BPCBS.

Thermochemical condition: Volume of aqueous and organic phase: 2.5×10^{-5} m^3 each, temperature: 323 K, MDEA concentration: 3.0 kmol/m^3, stirring speed: 1500 rpm, catalyst concentration: 6.0×10^{-3} kmol/m^3, sulfide concentration: 2.0 kmol/m^3.

The order of the reaction with respect to the p-CBC concentration was calculated by plotting a graph between ln (initial rate) and ln (reactant concentration). From the slope of the graph of Fig.4.5, the order of the reaction was found to be 1.58 with respect to catalyst concentration.

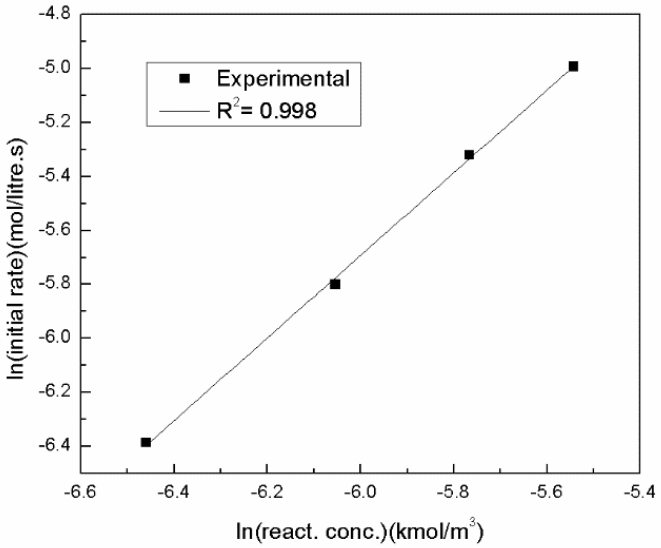
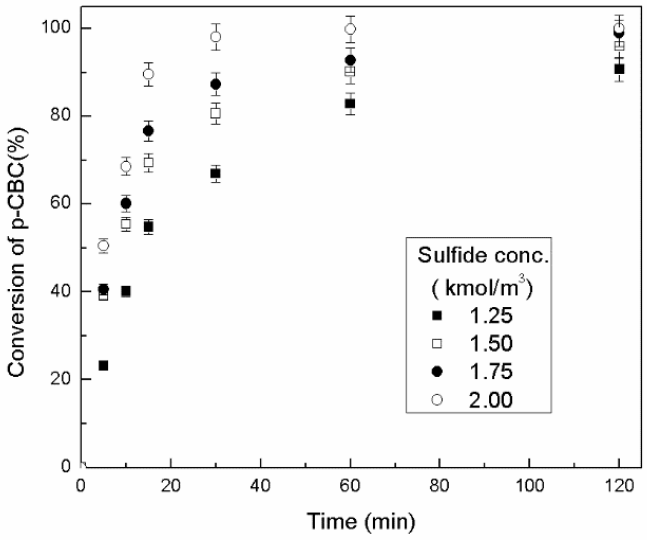


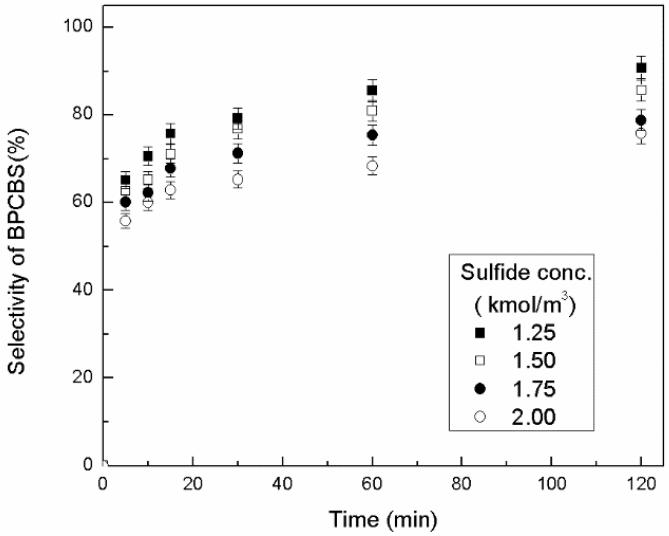
Fig. 4.5. Plot of ln (initial rate) vs. ln (reactant conc.) All conditions are same as mentioned under Fig. 4.4.

4.3.4. Effect of sulfide concentration

The sulfide concentration was varied between 2.0 kmol/m^3 to 1.25 kmol/m^3 keeping other parameters at an optimum value. The effect of the sulfide concentration on conversion of p-CBC and selectivity of BPCBS are shown in the Fig. 4.6 (a) and (b). From the graph, it can be interpreted that conversion of p-CBC decreases with a decrease in sulfide concentration as S^{2-} and HS^- ions present in limiting quantity. Selectivity of the BPCBS was found to decrease with increasing sulfide concentration because with an increase in total sulfide concentration, results in an increase in HS^- ion concentration in comparison to S^{2-} ion that leads to higher rate of formation of p-CBM, not BPCBS (Maity et al. 2009). As per stoichiometry Eq. (4.6)-(4.9) and Eq. (4.13)-(4.14) in Scheme 4.1, S^{2-} is more responsible for the formation of BPCBS than HS^-.



(a)



(b)

Fig. 4.6. Effect of sulfide concentration on (a) conversion of p-CBC and (b) selectivity of BPCBS.

Thermochemical condition: Volume of aqueous and organic phase: 2.5 $\times 10^{-5}$ m^3, temperature: 323 K, MDEA concentration: 3.0 kmol/m^3, stirring speed: 1500 rpm, catalyst concentration: 6.0 $\times$ 10^{-3} kmol/m^3, reactant concentration: 2.4 kmol/m^3.

The order of the reaction with respect to the sulfide concentration was calculated by plotting a graph between ln (initial rate) and ln (sulfide concentration). The slope of the

straight line in Fig.4.7 was calculated as 1.72 that is the order of the reaction with respect to sulfide concentration.

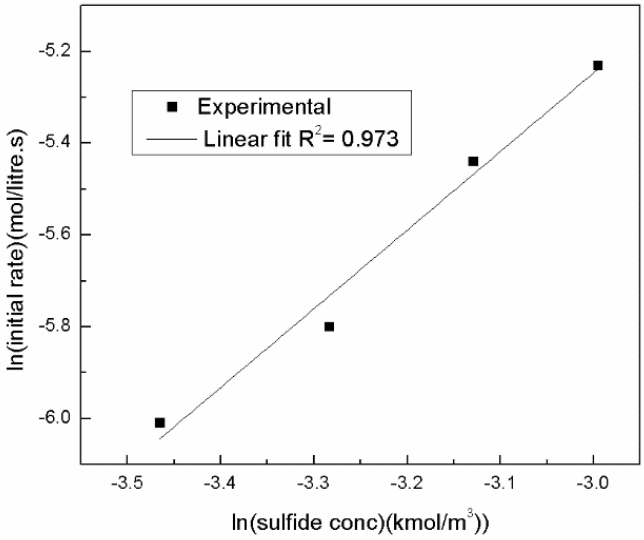
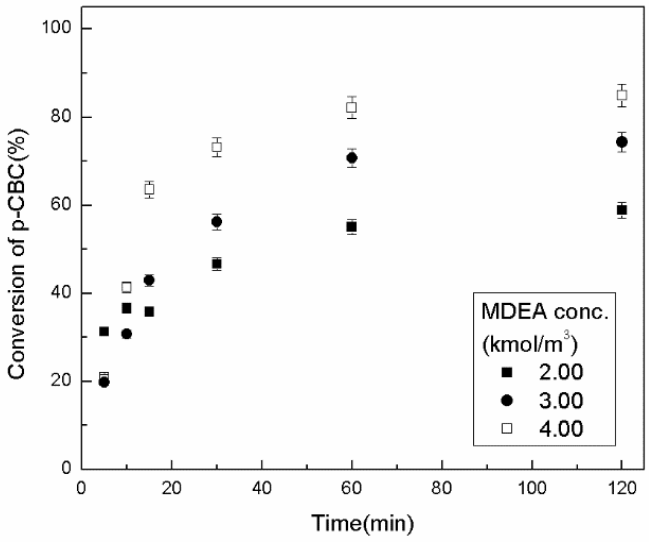


Fig. 4.7. Plot between ln (initial rate) and ln (sulfide conc.) All conditions are same as mentioned under Fig. 4.6.

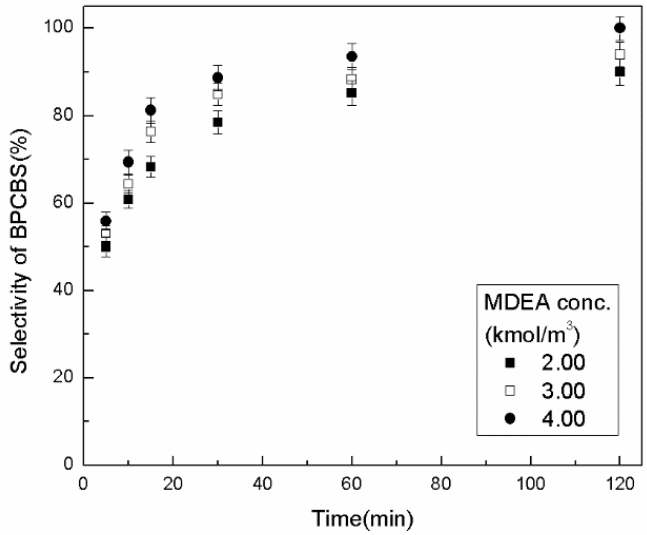
4.3.5. Effect of MDEA concentration

To study the effect of MDEA concentration on the kinetics of the reaction, MDEA concentration was varied keeping the sulfide concentration same for each case Fig. 4.8. For this experiment, we have taken fixed H_2S laden MDEA, and the concentration of MDEA was managed by adding the proper quantity of raw MDEA. Distilled water was used to make up the volume of aqueous phase if needed.

Even though MDEA doesn't take part in the reaction, the change in concentration of MDEA affects the conversion as well as selectivity. By changing the MDEA concentration the equilibrium between the MDEA, H_2O, S^{2-} and HS^- gets affected. When MDEA concentration is increased keeping H_2S concentration fixed, the equilibrium shifts towards the product side according to Le-Chatelier's principle, and that results in more RNH^+HS^- and $(RNH)_2S$ is formed. Therefore the conversion of p-CBC as well as the selectivity of BPCBS increase due to an increase of S^{2-} ion in comparison to HS^- with an increase in MDEA concentration (Maity et al. 2006).



(a)



(b)

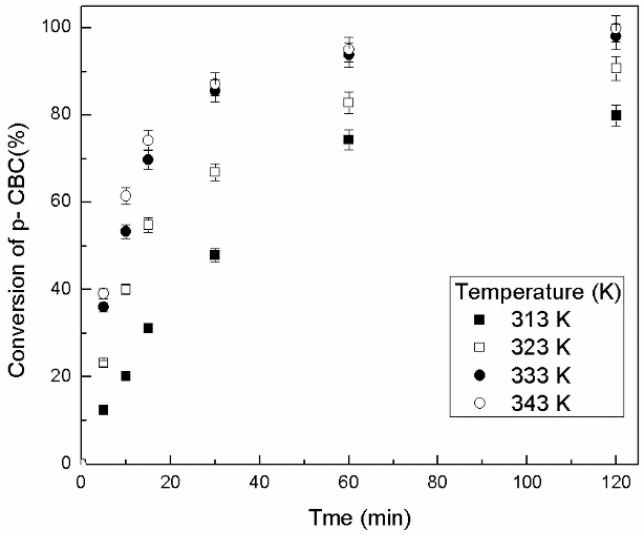
Fig. 4.8. The effect of MDEA concentration on conversion of reactant (a) and selectivity of the product (b).

Thermochemical condition: Volume of aqueous and organic phase: 2.5 $\times 10^{-5}$ m^3, temperature: 323 K, stirring speed: 1500 rpm, catalyst concentration: 6.0 $\times$ 10^{-3} $kmol/m^3$, reactant concentration: 2.4 $kmol/m^3$.sulfide concentration: 1.29 $kmol/m^3$.

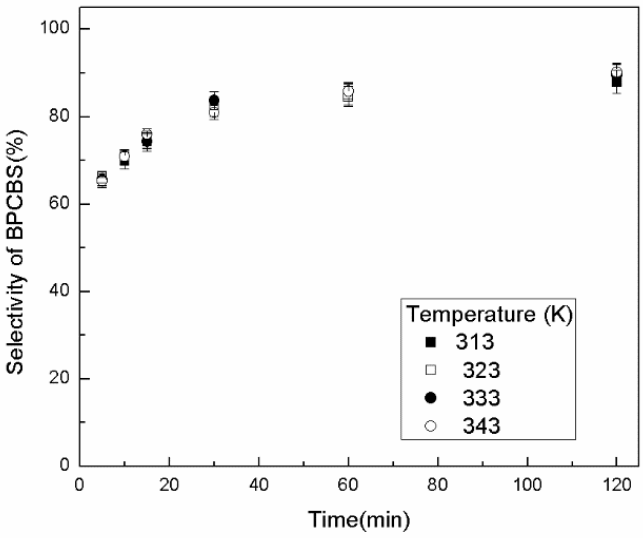
4.3.6. Effect of temperature

To study the effect of temperature, four set of experiments have been performed at different temperatures like 313, 323, 333 and 343 K, keeping other parameters constant. The graphical representation of p-CBC conversion and BPCBS selectivity vs. time for different temperatures are shown in the Fig. 4.9. From the graph, it is clearly understandable that the conversion (and rate of reaction) increases with increasing temperature as the number of particles colliding with sufficient energy (i.e. more than the activation energy) increases by increasing the temperature. But no significant effect on the selectivity of product BPCBS due to temperature change was observed.

The effect of temperature on chemical reactions is explained in the terms of activation energy in the Arrhenius Law. The colliding molecules should have sufficient energy to overcome the threshold energy i.e. activation energy for a successful reaction. The apparent activation energy was calculated from the slope of the Arrhenius plot (Fig. 4.10) as 34.86 kJ/mol.



(a)



(b)

Fig. 4.9. The effect of temperature on conversion of reactant (a) and selectivity of the product (b).

Thermochemical condition: Volume of aqueous and organic phase: 2.5 $\times 10^{-5}$ m^3 each, MDEA concentration: 3.0 kmol/m^3, stirring speed- 1500 rpm, catalyst concentration: 6.0 $\times$ 10^{-6} kmol/m^3, reactant concentration: 2.4 kmol/m^3, sulfide concentration: 2.00 kmol/m^3.

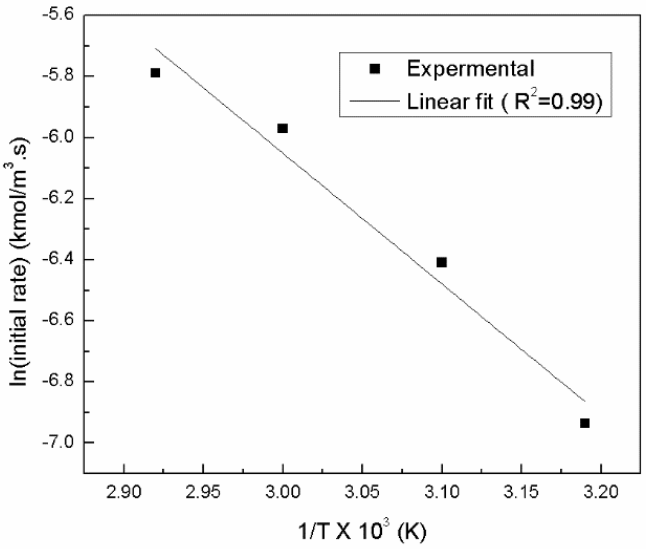
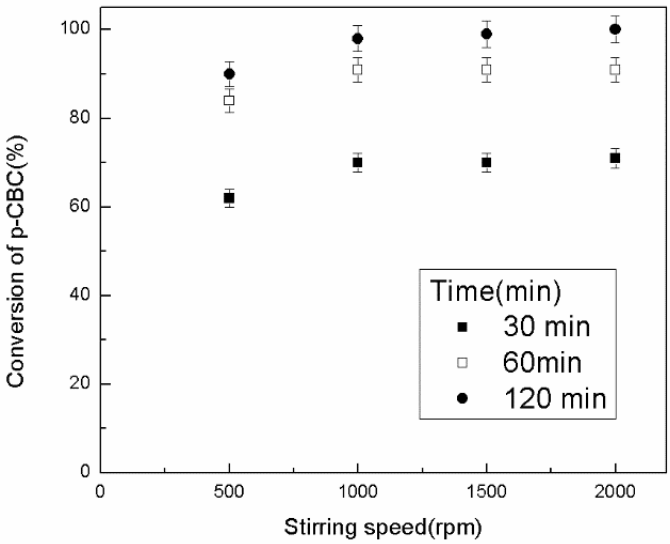


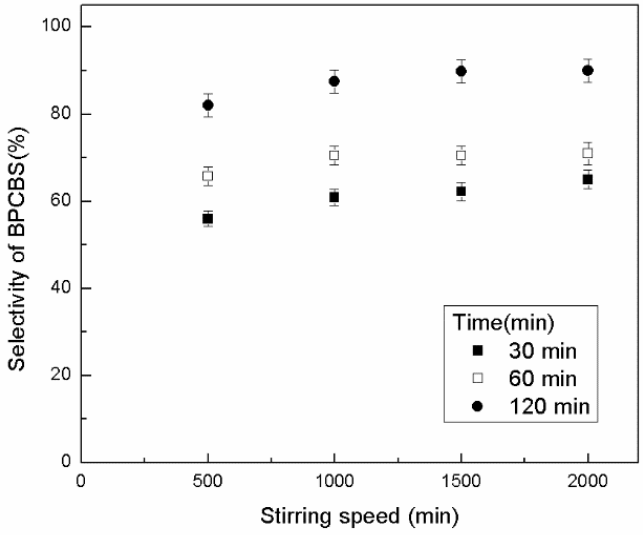
Fig. 4.10. Arrhenius plot of ln (rate of reaction) and 1/Temperature. All conditions are same as mentioned under Fig. 4.9.

4.3.7. Effect of stirring speed

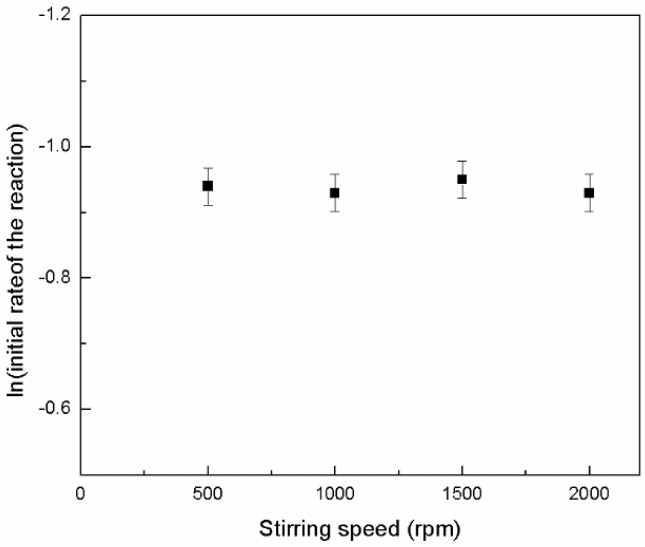
The stirring speed was varied in the range 500 - 2000 rpm keeping other parameters fixed at the optimized condition and the impact of the variation on the conversion of p-CBC and selectivity of BPCBS is shown in Fig.4.11. The conversion of p-CBC and selectivity of BPCBS after 30, 60 and 120 min is plotted against different stirring speed. From the Fig. 4.11, it is visually clear that role of mass transfer is negligible from 1000-2000 rpm. The conversion of p-CBC, as well as selectivity of BPCBS, is comparatively less at 500 rpm than 1000, 1500 and 2000 rpm. The relation between ln (initial rate of the reaction) and stirring speed is also plotted in Fig.4.11(c) which shows that there is no effect of agitation intensity on the initial rate of reaction. Therefore, to avoid mass transfer resistance, 1500 rpm was chosen as stirring speed for all above reactions conditions.


Conversion of p-CBC(%)
Stirring speed(rpm)
Time(min)
30 min
60min
120 min
0
20
40
60
80
100
0
500
1000
1500
2000

(a)


Selectivity of BPCBS(%)
Stirring speed (min)
Time(min)
30 min
60 min
120 min
0
20
40
60
80
100
0
500
1000
1500
2000

(b)



(c)

Fig. 4.11. The effect of stirring speed on (a) conversion of p-CBC and (b) selectivity of BPCBS (c) and ln (initial rate of the reaction).

Thermochemical condition: Volume of aqueous and organic phase: 2.5 $\times 10^{-5}$ m^3 each, temperature: 323 K, MDEA concentration: 3.0 kmol/m^3, catalyst concentration: 6.0 $\times$ 10^{-6} kmol/m^3, reactant concentration: 2.4 kmol/m^3, sulfide concentration of aqueous phase: 2.0 kmol/m^3.

4.3.8. Reusability of the catalyst

The major advantage of polymer-supported insoluble catalyst over other soluble L-L PTC catalysts is manifold. It is reusable in nature whereas other L-L PTC can't be reused, so polymer-bound catalyst can be used multiple times without much loss of its catalytic activity. It is also environment-friendly in nature. In the present study, after each run, the catalyst was separated using filtration and regenerated by washing it with NaCl solution. The reusability of the catalyst was examined up to two cycles and a little decrement in the conversion of p-CBC was observed i.e. from 100% for a fresh catalyst to 95% for 1st reuse and 91% for 2nd reuse. The conversion of p-CBC for 1st and 2nd cycle of reuse is as shown in the Fig.4.12. The reduction in the conversion can be attributed to the loss of little catalyst during filtration and regeneration.

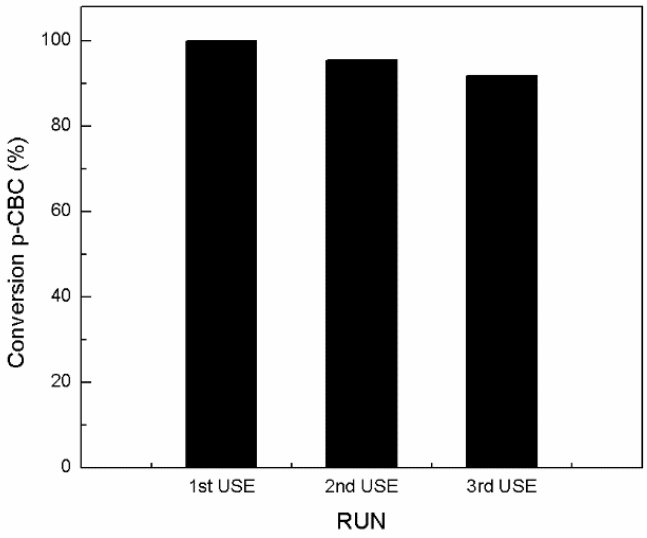


Fig. 4.12. Conversion of p-CBC with the number of cycle reuse.

Thermochemical condition: Volume of aqueous and organic phase: 2.5 $\times 10^{-5}$ m^3 each, MDEA concentration: 3.0 kmol/m^3, temperature: 323 K, stirring speed- 1500 rpm, sulfide concentration: 1.29 kmol/m^3, catalyst concentration: 6.0 $\times$ 10^{-3} kmol/m^3, reactant concentration: 2.4 kmol/m^3.

4.4. Kinetic Modeling

4.4.1. Development of kinetic model

The model for the synthesis of DBS in L-L mode of reaction is also not found to be applicable in L-L-S mode of reaction because solid catalyst does not get distributed in both the phases (Maity et al. 2009). There is various literature available for different the type of reaction of L-L (Yang and Huang 2006; Yadav and Jadhav 2003), L-L-L (Yadav and Badure 2007; Yadav and Naik 2001), L-L-S PTC-driven reactions (Singh et al. 2016) where authors have developed and applied their kinetic model. But the model for L-L-S mode of synthesis of any thioethers or ethers is not available in the literature.

From Fig.4.2, it can easily be interpreted that non-catalytic contribution in this reaction rate is unavoidable. The rate equation (Eq. (4.17)) thus comprises of two terms - first one is accountable for catalytic reaction and dependents on concentration of reactant (C_{R1}), sulfide (C_{S1}) and catalyst (C_C) and second term is for non-catalytic reaction and dependents on concentration of reactant (C_{R2}) and sulfide (C_{S2}) only [Eq. (4.17)]. Non-catalytic reactions at different temperatures - 313, 323, 333 and 343 K were carried out to estimate k_2 from Eq. (4.17). The effect of temperature change in the catalytic as well as

non-catalytic part of the reaction is shown in terms of Arrhenius plot in the Fig. 4.13(a) and (b) respectively. Here it was assumed that the contribution of reactant concentration and sulfide concentration to rate of reaction for non-catalytic reaction is same as catalytic reaction. Thus, order of reaction for catalytic and non-catalytic reaction are assumed to be same.

$$-r = k_1 C_{R1}^{1.58} C_{S1}^{1.72} C_C^{0.62} + k_2 C_{R2}^{1.58} C_{S2}^{1.72} \quad (4.16)$$

The overall mass balance for sulfide can be obtained from the stoichiometric equations Eq. (4.9), (4.10), (4.11) and (4.13) and is given by Eq. (4.17).

$$C_S = C_{S0} - 1/2f(C_{R0}\text{-}C_R) \quad (4.17)$$

Where, C_{R0} and C_{S0} are initial concentration of p-CBC and sulfide and f is the ratio of volume of organic phase to that of aqueous phase.

A nonlinear regression algorithm is used for the estimation of parameters. The optimum values of the rate constants, k_1 and k_2 were estimated by minimizing the objective function (E) as given by the following equation:

$$E = \sum_{i=1}^{n} [\{(-r_R)_{pred}\}_i - \{(-r_R)_{expt}\}_i]^2 \quad (4.18)$$

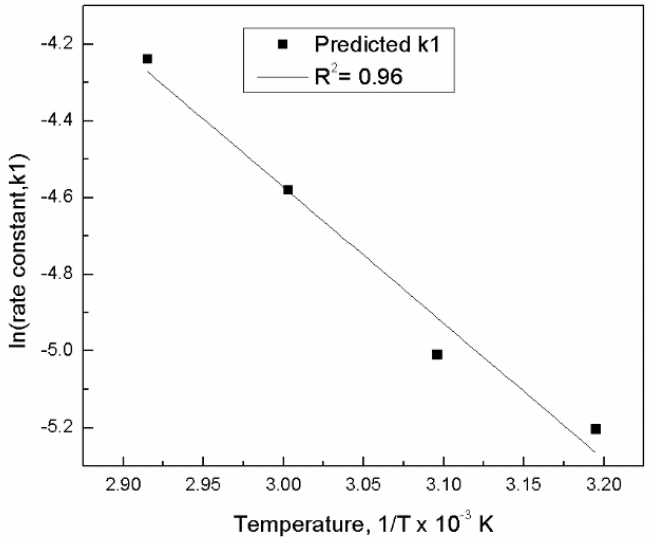
The optimum values of rate constant k_1 and k_2 of the reaction for different temperatures were listed the table below:

Table 4.2.

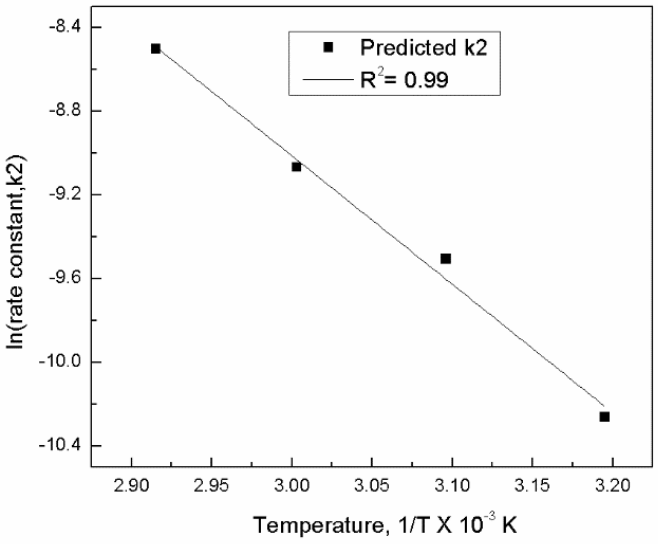
Rate Constants of the Model

Temperature (k)	Rate constant (with catalyst) $\boldsymbol{k_1}$(($kmol/m^3$)$^{-4}$.s^{-1})	Rate constant (without catalyst) $\boldsymbol{k_2} \times 10^5$(($kmol/m^3$)$^{-4}$.$s^{-1}$)
313	0.001264	3.496
323	0.005190	7.439
333	0.010246	11.542
343	0.013381	20.333

From its slope of Fig. 4.13 (a) and (b), the activation energy for the catalytic and non-catalytic reaction was found to be 28.89 kJ/mol and 49.96 kJ/mol respectively, which also shows the effectiveness of the catalyst.



(a)



(b)

Fig. 4.13. Arrhenius plot, (a) ln (rate constant, k_1) vs temperature (1/T) and (b) ln (rate constant, k_2) vs temperature (1/T)

4.4.2. Validation of the Kinetic Model

From the regression of the model, the predicted values for reaction rate were found. Using those values, the predicted conversions are compared with experimentally calculated values of conversion. An excellent agreement between the predicted and experimental conversion was found as shown in the Fig.4.14.

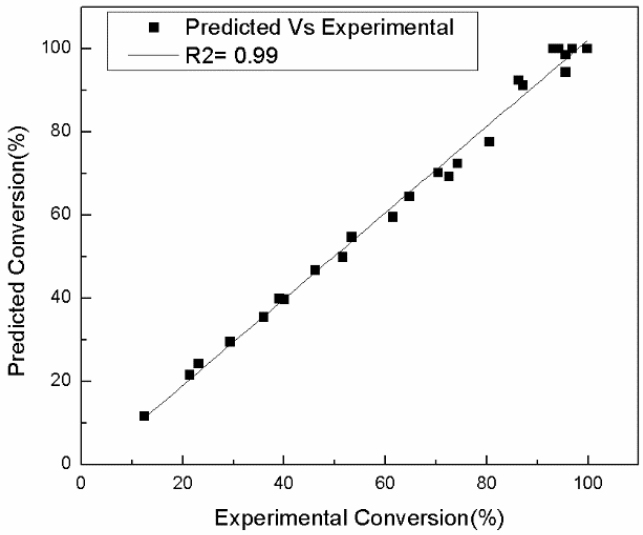


Fig. 4.14. Comparison of Model-predicted p-CBC conversion with the experimental p-CBC conversion.

4.5. GC-FID and GC-MS spectra

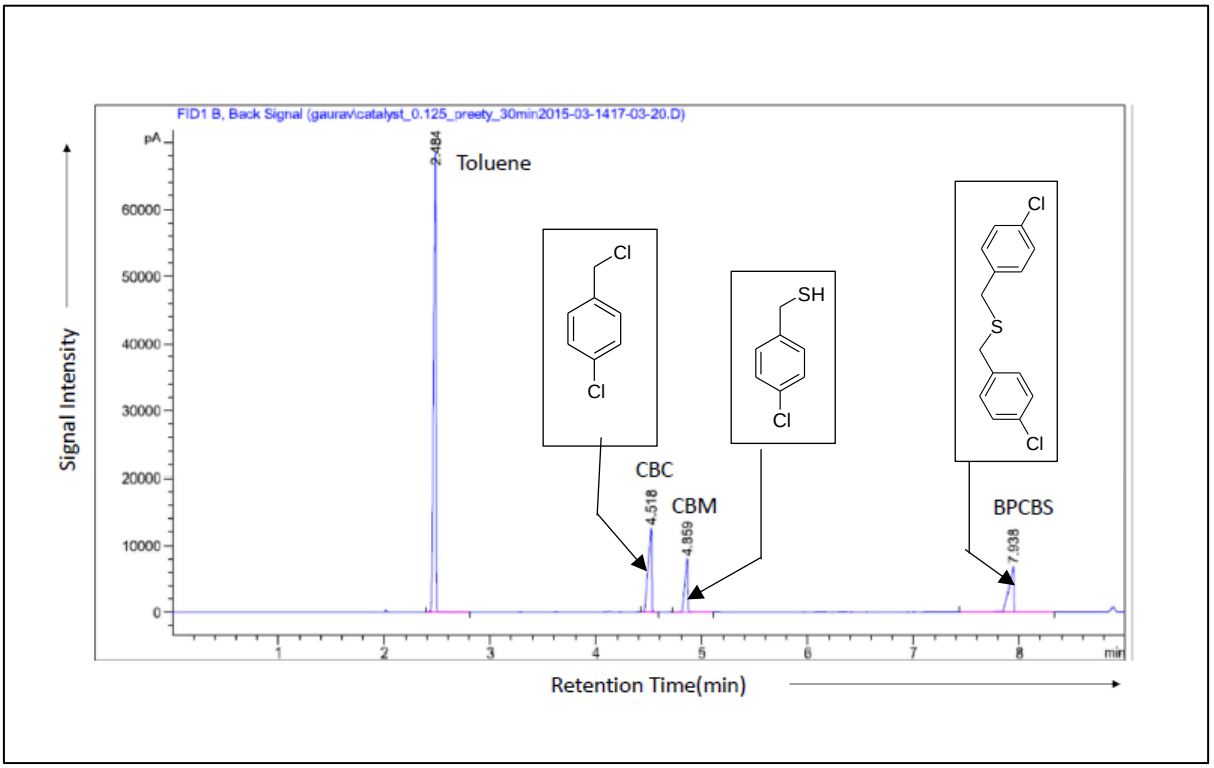


Fig. 4.15: GC spectra showing the formation of Bis-(p-chlorobenzyl) Sulfide from reactant p-chlorobenzyl chloride in solvent toluene.

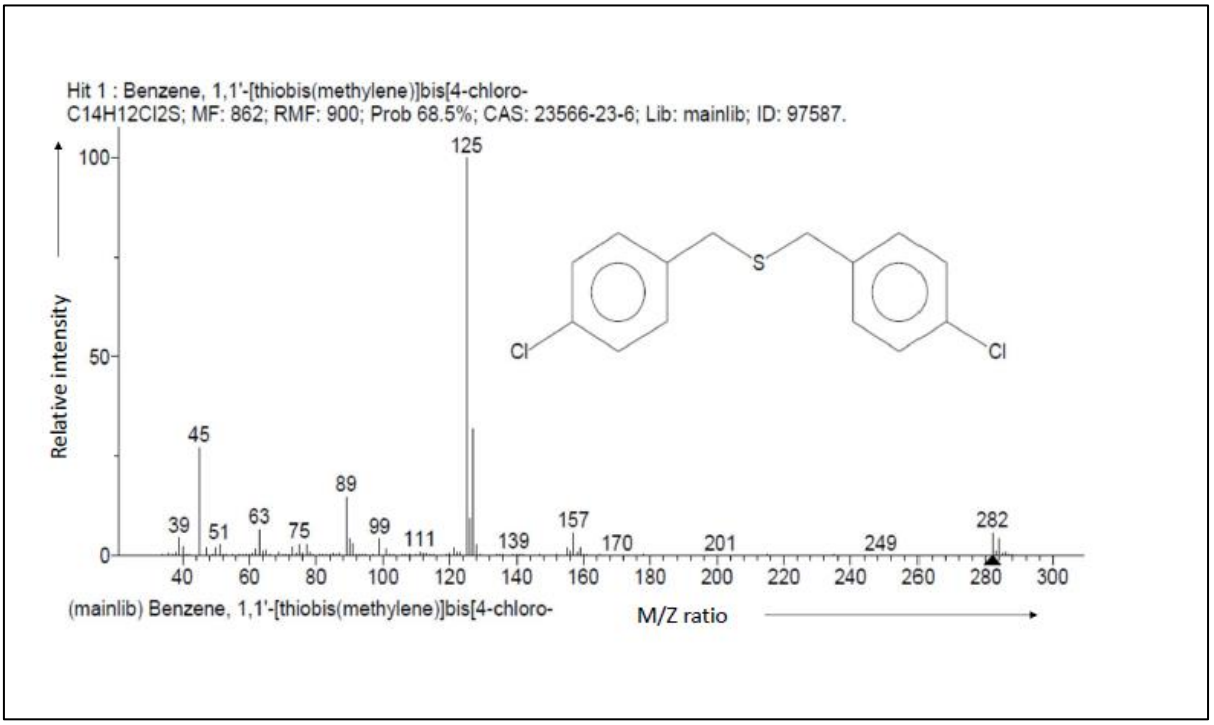


Fig. 4.16: Mass spectra of the product Bis-(p-chlorobenzyl) Sulfide

CHAPTER 5

Dual Optimization in Synthesis of Bis-(p-chlorobenzyl) Sulfide

5.1. Introduction

A protocol, to utilize sour gas H_2S by synthesis of value-added fine chemicals i.e. Bis-(p-chlorobenzyl) sulfide, has been developed, and the conditions for the reaction have also been optimized. H_2S absorbed in aqueous N-methyldiethanolamine was used to synthesize bis-(p-chlorobenzyl) sulfide using polymer-bound Tributylmethylphosphonium chloride catalyst as phase transfer catalyst in the liquid-liquid-solid mode of catalysis. Response surface methodology accompanied with Central composite design was employed for the study of the reaction kinetics, model development and the optimization of the reaction conditions. Two products were found - bis-(p-chlorobenzyl) sulfide (BPCBS) and p-chlorobenzyl mercaptan and conversion of p-CBC and selectivity of BPCBS have been chosen as the dual responses.

We have used the design of experiments for the dual optimization of conversion of the reactant p-CBC and selectivity of the product BPCBS. Using this model we have studied the effect of different parameters that alter the conversion of p-CBC and selectivity of the BPCBS. Optimization of different parameters for maximizing conversion and selectivity has also been successfully employed.

5.2. One-variable-at-a-time approach

For the optimization of outcomes (e.g. conversion, selectivity, and yield), experimentalists have been using the method of changing one variable at a time (OVAT) and keeping other parameters constant for many years. But OVAT process of optimization was accompanied with some disadvantages. When more than one factor is accountable for the calculation of outcome, OVAT can’t be used for the precise result as the results are accompanied by some error. Besides this problem OVAT is time consuming and expensive too (Yuan et al. 2008). So the method of varying more than one variable at a time like Surface Response Methodology (RSM) can be used for optimization of outcomes with minimal error.

5.3. Results and discussion

5.3.1. Proposed Mechanism

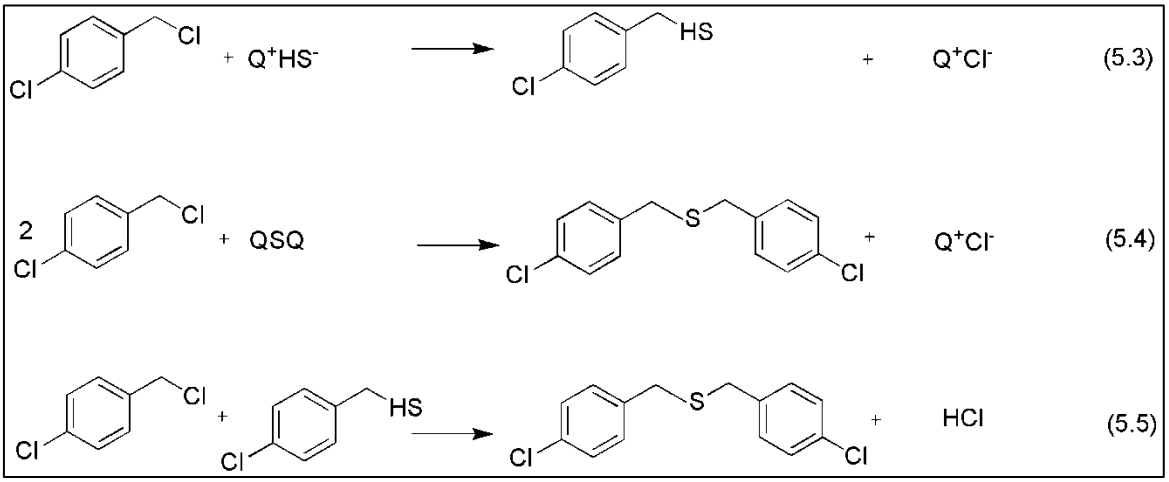
The mechanism for polymer-supported catalyst was firstly developed and explained by desikan and Doraiswamy (Desikan & Doraiswamy 1995). According to this mechanism, movement of the solid PSC is restricted in the interphase of the reaction and reactants need to be brought into contact with the catalyst in a sequential manner. The reaction takes place through the attachment and detachment of ions of aqueous and organic phase on the active sites of the catalyst.

For the proposed work, H_2S, absorbed in MDEA is reacted with p-chlorobenzyl chloride (p-CBC) in the presence of tributylmethylphosphonium chloride as PSC and toluene as solvent. The mechanism of the reaction follows L-L-S mode that is very complex. H_2S, H_2O, and MDEA react with each other to form ions like HS^-, S^{2-}, which being nucleophilic in nature, migrates from the aqueous phase to the vicinity of the inactive sites of the catalyst. The attachment to the catalyst is followed by ion exchange reaction between the nucleophile and the inactive site of the catalyst and leaving the catalyst site active intermediate state, i.e., Q^+HS^-, QSQ. The ion exchange reaction stoichiometric equation is as shown in the equations 1 and 2.

$$Q^+Cl^- + HS^- \rightarrow Q^+HS^- \quad (5.1)$$

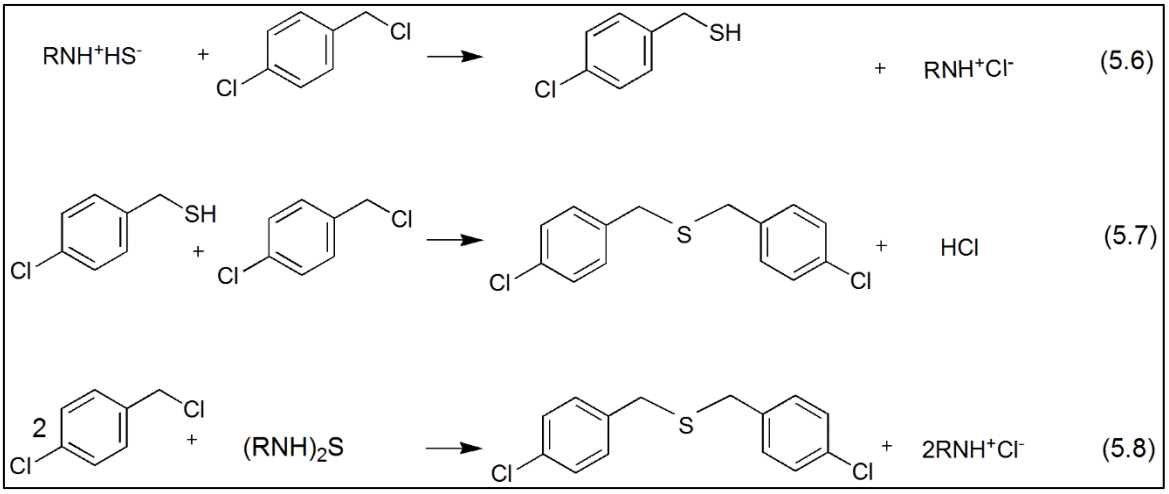
$$2Q^+Cl^- + S^{2-} \rightarrow QSQ \quad (5.2)$$

The organic substrate RX, p-CBC, diffuses to the bulk of organic phase to the active sites of the catalyst i.e. Q^+HS^- and QSQ to form products p-chlorobenzyl mercaptan (p-CBM) and bis-(p-chlorobenzyl) sulfide (BPCBS) as shown in the **Scheme 5.1**.



Scheme 5.1: The reaction of catalyst active sites with the organic phase to form product p-chlorobenzyl mercaptan and bis-(p-chlorobenzyl) sulfide.

But due to the presence of a solvent and continuous stirring, some reactions follows non-catalytic path too which is unavoidable. The reaction of H_2S, H_2O and MDEA form ionic intermediates RNH^+HS^- and $(RNH)_2S^-$. These ionic intermediates react with p-CBC to form products p-CBM and BPCBS as shown in the equations of following **Scheme 5.2.**

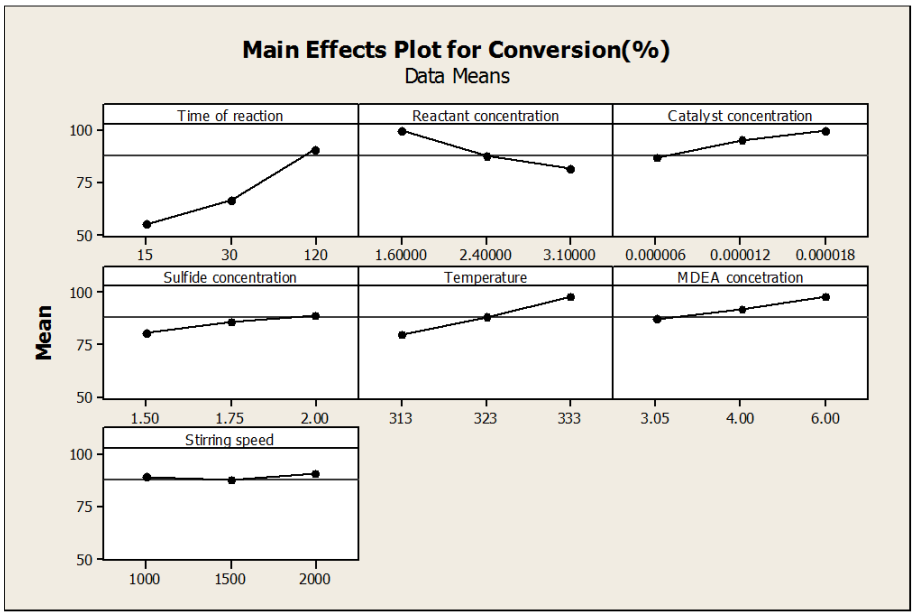


Scheme 5.2: Non-catalytic reaction to form products p-chlorobenzyl mercaptan and bis-(p-chlorobenzyl) sulfide.

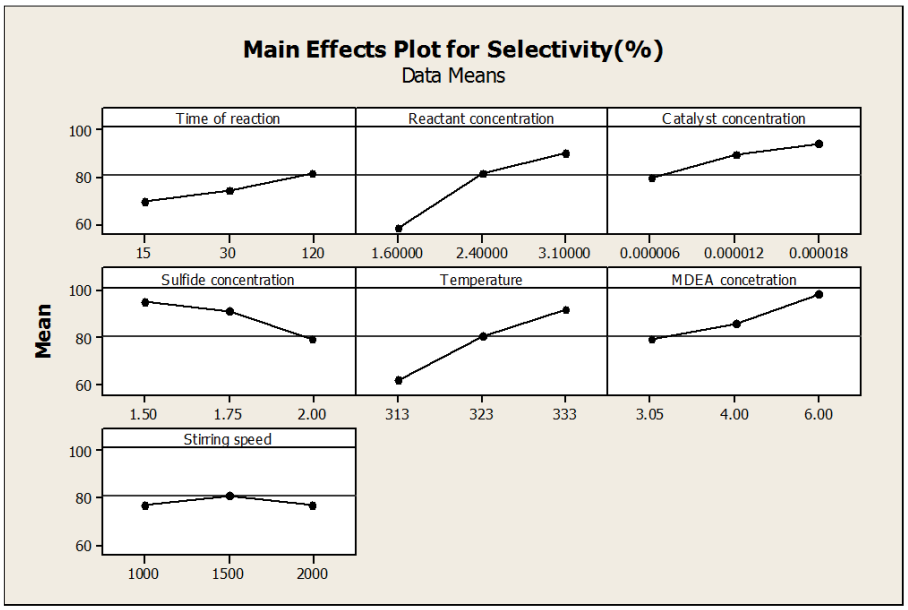
5.3.2. Multivariate experiment design

Concentrations of reactant p-CBC, sulfide, catalysts, time, and temperature of the reaction are the parameters that affect the response conversion of p-CBC and selectivity of BPCBS insignificant. The slope of the plot is a measure to determine the extent of effect due to the individual parameter on the response. Stirring speed, beyond 1000 rpm, doesn't play a significant role on reaction kinetics (Fig 5.1). For the parameter, time has a significant effect on the rate of reaction but only till 120 min, thus, time as a parameter can be eliminated by keeping it constant as 120 min for all the run of the experiment.

There is some mass transfer effect on the reaction when the stirring speed is less than 1000 rpm, but mass transfer effect plays an insignificant role when the stirring speed goes beyond 1000 rpm. So for all the reaction we have kept the stirring speed as 1500 rpm and run time of the reaction as 120 min. From the Fig 5.1, it is easy to interpret that the concentration of catalyst, reactant, and temperature of the reaction affect the response to a greater extent. Reactant concentration has a negative effect on the conversion of the p-CBC and sulfide concentration has a negative impact on the selectivity of the product BPCBS.



(a)



(b)

Fig 5.1: Main effect plot on (a) conversion of p-CBC and (b) selectivity of BPCBS of different parameters.

5.3.3. Development of regression model Equation

Response surface methodology with the central composite design was used to optimize the conversion of p-CBC and selectivity of BPCBS and its relative interactions with catalyst concentration, reactant concentration, sulfide/MDEA ratio and temperature. By taking the parameters in range as shown in Table 5.1 design of experiments generates experimental design matrix Table 5.2 that comprises of 30 experimental runs. The quadratic equation model is suggested the best for the by the software for the provided data based on the best lack of fit test, favorable F value, "prob>F" value, standard deviation and R^2 value, is shown in the form of the quadratic polynomial equation given above.

Table 5.1 The range of the values for various parameters taken for the experiment

				Parameters	
Level	code	Temperature (K)	Catalyst concentration ($\times 10^6$ kmol/m^3)	Reactant concentration ($\times 10^3$ kmol/m^3)	MDEA/Sulfide ratio
lowest	-2	303	7	1.571	1.271
low	-1	313	14	2.347	1.525
mid	0	323	21	3.124	1.779
high	1	333	28	3.900	2.033
highest	2	343	35	4.677	2.287

Table 5.2: Experimental design matrix and results - A 2^4 full factorial CCD with six replicates of the Centre point

	Different Parameters				Response	
Run	A:Temp (K)	B: Catalyst conc. ($\times 10^6$ kmol/m^3)	C: Reactant conc. ($\times 10^3$ kmol/m^3)	D:MDEA /Sulfide	Conversion of p-CBC (%)	Selectivity of BPCBS (%)
1	313	28	3.900	1.525	85.17	92.29
2	323	7	3.124	1.779	78.16	87.53
3	323	21	3.124	1.779	91.81	95.63
4	313	28	3.900	2.033	77.74	100.00
5	313	14	3.900	1.525	80.14	92.11
6	323	21	3.124	1.779	89.81	96.63
7	333	28	2.347	2.033	98.72	100.00
8	303	21	3.124	1.779	86.84	89.26
9	313	14	3.900	2.033	69.16	100.00
10	313	28	2.347	2.033	97.35	94.67
11	343	21	3.124	1.779	82.77	90.00
12	313	14	2.347	1.525	90.98	84.80
13	333	28	3.900	1.525	83.32	98.45
14	333	28	2.347	1.525	90.00	97.00
15	323	21	3.124	1.779	90.81	97.63
16	323	21	3.124	1.779	92.81	96.87
17	333	14	2.347	1.525	80.00	81.87
18	323	21	3.124	2.287	84.69	100.00
19	333	28	3.900	2.033	83.51	100.00
20	333	14	2.347	2.033	85.97	82.90
21	333	14	3.900	1.525	79.00	86.34
22	323	21	3.124	1.779	92.81	96.89
23	323	21	4.677	1.779	73.00	97.00
24	313	14	2.347	2.033	85.99	92.69
25	313	28	2.347	1.525	100.00	82.98
26	333	14	3.900	2.033	75.40	87.00
27	323	21	3.124	1.271	89.93	87.49
28	323	21	3.124	1.779	91.20	96.10
29	323	21	1.571	1.779	100.00	84.31
30	323	35	3.124	1.779	100.00	100.00

From the theory of statistics, CCD performed for four parameters at five levels includes sixteen standard factorial runs, eight axial runs, and six central runs. After the experiments had been done, the two response variables (conversion and selectivity) was fitted with second order model in the following quadratic polynomial equation (5.9).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (5.9)$$

Where Y is the response of dependent variable (p-CBC conversion or selectivity of BPCBS in this case), β_0 is constant, β_i is regression coefficient for linear effects, β_{ii} is quadratic coefficient, β_{ij} is interaction coefficient and x_i & x_j are independent variables that influence the response.

The analysis has been focused on the influence of four independent variables, i.e. temperature (A), catalyst concentration (B), reactant concentration (C) and MDEA/sulfide ratio (D). The mathematical relation for conversion of p-CBC and selectivity of BPCBS. So the final regression model for p-CBC conversion developed by the RSM in terms of coded factors has been expressed by the following second order polynomial equation (5.10).

$$\%\, X_{P-CBC} = 91.54 - 0.78A + 4.7B - 6.23C - 1.05D + 0.075AB + 1.79AC + 2.33AD - 1.07BC + 0.78BD - 1.8CD - 1.98A^2 - 0.91B^2 - 1.56C^2 - 1.35D^2 \quad (5.10)$$

Final model equation (13) for p-CBC conversion in terms of actual factors (subjected to the range shown in Table 5.1) has been obtained as follows:

$$\%\, conversion\ p-CBC = -1310.155 + 10.335A + 0.945B - 45.994C - 206.665D + 0.001AB + 0.231AC + 0.918AD - 0.196BC + 0.436\,BD - 9.147CD - 0.0198A^2 - 0.0185B^2 - 2.580C^2 - 20.976D^2 \quad (5.11)$$

Similarly, the final regression model for the selectivity of BPCBS developed by the RSM in terms of coded factors has been expressed by following polynomial equation (14).

$$\%\, Y_{BPCBS} = 96.62 - 0.19A + 3.44B + 2.69C + 2.77D + 3.56AB - 1.20AC - 1.81AD - 0.44BC + 0.41BD - 0.36CD - 1.73A^2 - 0.69B^2 - 1.47C^2 + 0.70D^2 \quad (5.12)$$

Final model equation (15) for the selectivity of BPCBS in terms of actual factors (subjected to the range shown in Table 5.1) has been obtained as follows:

$$\%\, Selectivity\ of\ BPCBS = -2033.377 + 11.832A - 15.500B + 73.728C + 280.478D + 0.050AB - 0.154AC - 0.712AD - 0.081BC + 0.227BD - 1.839CD - 0.017A^2 - 0.014B^2 + 2.441\,C^2 - 10.842D^2 \quad (5.13)$$

5.3.4. Analysis of variance (ANOVA) and model adequacy test

Analysis of variance is used to study the significance of the model. Therefore, an ANOVA has been conducted to generate the sum of squares, the degree of freedom (df), mean squares, F values, and p values by fitting the second order polynomial equation from the experimental data (Table 5.2). The results for the % conversion of p-CBC and selectivity of BPCBS are shown below in Table 5.3 and Table 5.4 respectively. As we know that a corresponding variable is more significant if its absolute p-value is smaller than 0.05. So except the model term AB and BD all other model effect terms were determined to be significant as per the standard. High degree of the precession of the experiments was confirmed on the basis of low coefficient of variation which was found to be CV=1.87 % and 1.09 % for conversion of p-CBC and selectivity of BPCBS respectively. This signifies the effectiveness of fit of the regression model. Adequate precision was found to be around 27 which is very high as compared to 4, so the model can be used to navigate the design space (Liu, Jing; Yan, Min; Yong-Kui Zhang; Du 2011).

The reliability of the proposed mechanism also depends on upon the agreement between the observed and predicted values. For the conversion of p-CBC, the predicted and observed conversion values are compared in Fig. 5.2 and the same for the selectivity of BPCBS is presented in Fig. 5.3. From both of the figures it is clear that the points clustered around the diagonal line with predicted R^2 and adjusted R_a^2 were very close (see Fig.5.2 and Fig.5.3). This symbolizes that the predicted values match well with the observed values and regression model exhibit an excellent stability. Thus, the model obtained by the regression successfully explains the most of the variability in the conversion of p-CBC and the selectivity of BPCBS in the given domain of experiments.

Table 5.3: For response surface quadratic model for p-CBC conversion

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	1902.54	14	135.90	51.28	< 0.0001	significant
A-Temperature	*14.68*	*1*	*14.68*	*5.54*	*0.0327*	
B-Catalyst conc	*530.49*	*1*	*530.49*	*200.17*	*< 0.0001*	
C-Reactant conc.	*931.99*	*1*	*931.99*	*351.67*	*< 0.0001*	
D-MDEA/Sulfide	*26.59*	*1*	*26.59*	*10.03*	*0.0064*	
AB	*0.089*	*1*	*0.089*	*0.034*	*0.8569*	
AC	*51.31*	*1*	*51.31*	*19.36*	*0.0005*	
AD	*87.02*	*1*	*87.02*	*32.83*	*< 0.0001*	
BC	*18.27*	*1*	*18.27*	*6.89*	*0.0191*	
BD	*9.64*	*1*	*9.64*	*3.64*	*0.0758*	
CD	*52.08*	*1*	*52.08*	*19.65*	*0.0005*	
A^2	*107.52*	*1*	*107.52*	*40.57*	*< 0.0001*	
B^2	*22.74*	*1*	*22.74*	*8.58*	*0.0104*	
C^2	*66.38*	*1*	*66.38*	*25.05*	*0.0002*	
D^2	*50.23*	*1*	*50.23*	*18.95*	*0.0006*	
Residual	39.75	15	2.65			
Lack of fit	*32.81*	*10*	*3.28*	*2.36*	*0.1773*	*not significant*
Pure error	*6.94*	*5*	*1.39*			
Cor Total	1942.29	29				

Table 5.4: For response surface quadratic model for selectivity of BPCBS

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	1058.38	14	75.60	73.83	< 0.0001	significant
A-Temperature	*0.84*	*1*	*0.84*	*0.82*	*0.3794*	
B-Catalyst conc	*284.45*	*1*	*284.45*	*277.80*	*< 0.0001*	
C-Reactant conc.	*174.20*	*1*	*174.20*	*170.14*	*< 0.0001*	
D-MDEA/Sulfide	*183.95*	*1*	*183.95*	*179.65*	*< 0.0001*	
AB	*203.03*	*1*	*203.03*	*198.29*	*< 0.0001*	
AC	*23.14*	*1*	*23.14*	*22.60*	*0.0003*	
AD	*52.36*	*1*	*52.36*	*51.14*	*< 0.0001*	
BC	*3.15*	*1*	*3.15*	*3.08*	*0.0996*	
BD	*2.63*	*1*	*2.63*	*2.57*	*0.1300*	
CD	*2.11*	*1*	*2.11*	*2.06*	*0.1721*	
A^2	*81.99*	*1*	*81.99*	*80.07*	*< 0.0001*	
B^2	*13.23*	*1*	*13.23*	*12.92*	*0.0027*	
C^2	*59.43*	*1*	*59.43*	*58.05*	*< 0.0001*	
D^2	*13.42*	*1*	*13.42*	*13.11*	*0.0025*	
Residual	15.36	15	1.02			
Lack of fit	*12.95*	*10*	*1.30*	*2.69*	*0.1430*	*not significant*
Pure error	*2.41*	*5*	*0.48*			
Cor Total	1073.74	29				

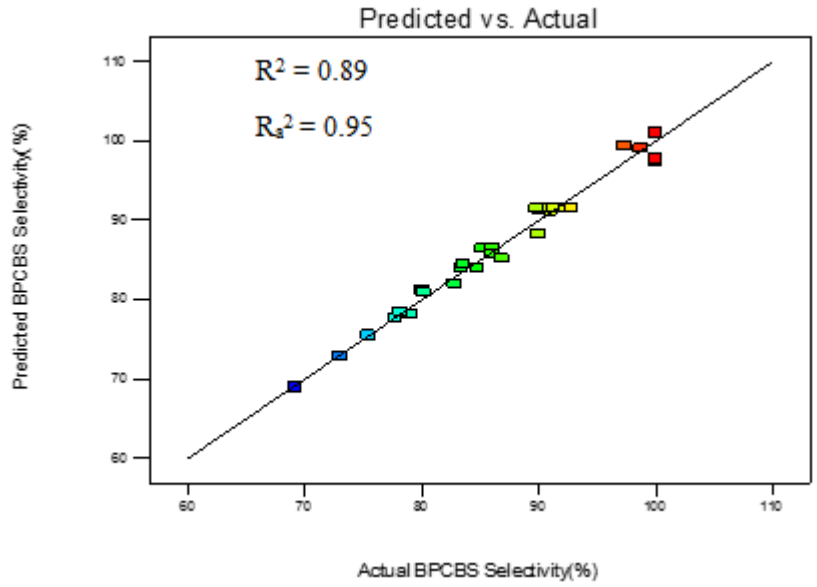


Fig. 5.2: Comparison between the predicted and actual % conversion of p-CBC.

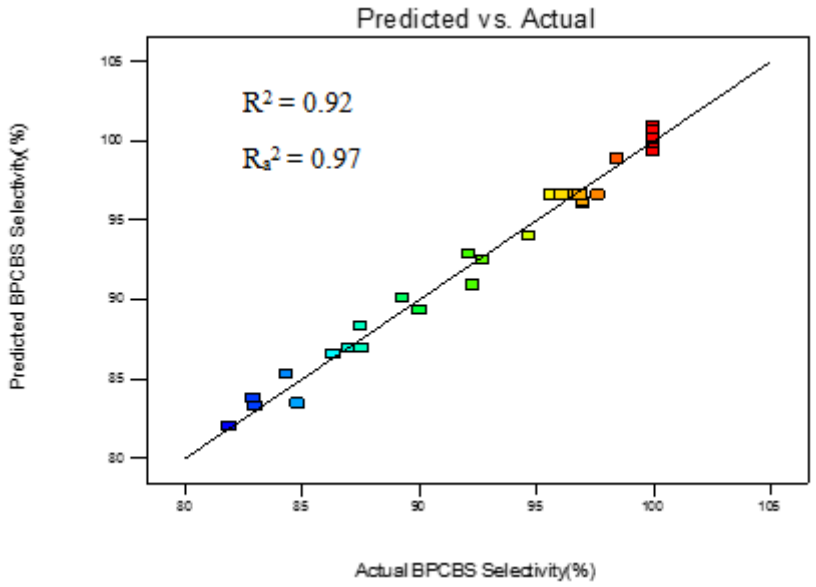


Fig. 5.3: Comparison of the predicted and actual % selectivity of BPCBS.

5.3.5. Effects of model components on the conversion p-CBC and their interaction

For the p-CBC conversion, all the variables are significant as the p-value is less than 0.01 except for the temperature of the reaction as its p-value is 0.0327 which is greater than 0.01. From the coefficient estimate, the effect of different variables on the responses i.e. conversion of p-CBC and selectivity of BPCBC can be understood. If the coefficient

estimate is positive for a variable, then the response increase with an increase in the value of the variable and vice versa. So from the from the coefficient estimate it is clear that catalyst concentration, temperature, and MDEA/Sulfide ratio have a positive effect on the conversion of p-CBC. Reactant concentration has the most significant role in the conversion of p-CBC, but the effect is negative as the coefficient estimate is negative. Then catalyst concentration plays a vital role in the enhancement of the rate of reaction.

The study of 3D plot and contour plot (Fig. 5.4 and Fig. 5.5) gives us a clearer interpretation of the effect of variables interaction on p-CBC conversion and BPCBS selectivity. 3D surface plot helps to understand the effect of single or combined effect of variables on the response, on the other hand, contour-plot helps to know the major interaction of variables with the response on the basis of nature of curve i.e. circular or elliptical.

The increase in conversion of p-CBC was observed with increase in the concentration of the catalyst, temperature, and the MDEA/Sulfide ratio. The reaction among H_2S, MDEA and H_2O forms ions like HS^-, S^{2-} and OH^- which combines with catalyst (Q^+Cl^-) to form catalyst active intermediates QSQ and QSH that combines with p-CBC to form BPCBS and p-CBM. Thus, with an increase in catalyst concentration, the concentration of these intermediate increases and hence the conversion of p-CBC and selectivity of BPCBS also increases.(Sujit Sen 2011) To change MDEA/Sulfide ratio, the MDEA concentration was kept unchanged, and sulfide concentration was decreased to increase the ratio. As the conversion of p-CBC decreases with a decrease in sulfide concentration as S^{2-} and HS^- ions present in limiting quantity and selectivity of the BPCBS was found to decrease with increasing sulfide concentration because with an increase in total sulfide concentration, results in an increase in HS^- ion concentration in comparison to S^{2-} ion that leads to higher rate of formation of p-CBM, not BPCBS (Maity et al. 2009). The temperature effect on conversion is less as compared to catalyst concentration, but it little increases the conversion of the reactant because with increasing temperature as the number of particles colliding with sufficient energy (i.e. more than the activation energy) increases by increasing the temperature. The reactant concentration has a significant role in decreasing the conversion of p-CBC when its concentration is increased. This happens due to the presence of a limited amount of S^{2-} and HS^- ions in the aqueous phase. For the maximum conversion i.e. 100% the optimum conditions are temperature: 328.53 K, catalyst concentration: 2.79×10^{-5} kmol/m^3, reactant concentration, 2.53×10^{-3} kmol/m^3, MDEA/Sulfide ratio: 2.08.

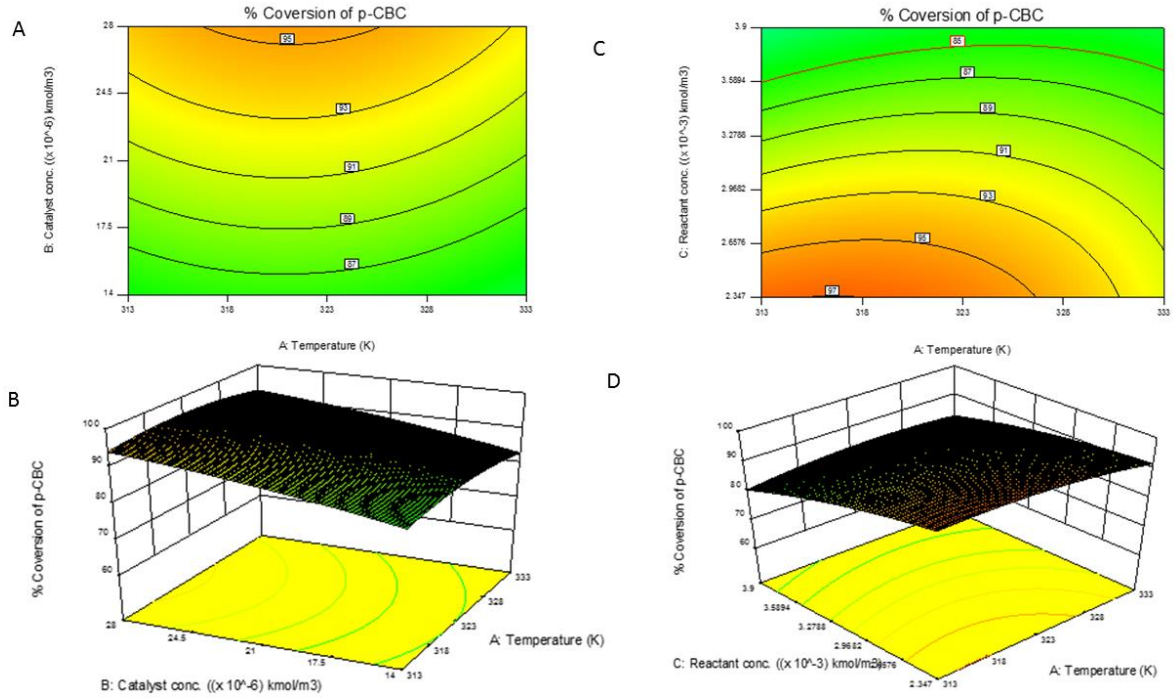


Figure 5.4: The effect and interaction of different independent variables for the response % conversion of p-CBC (A) Counter-plot of interaction of catalyst concentration and temperature (B) 3D surface plot of interaction of catalyst concentration and temperature (C) Counter-plot of interaction of reactant concentration and temperature (D) 3D surface plot of interaction of reactant concentration and temperature.

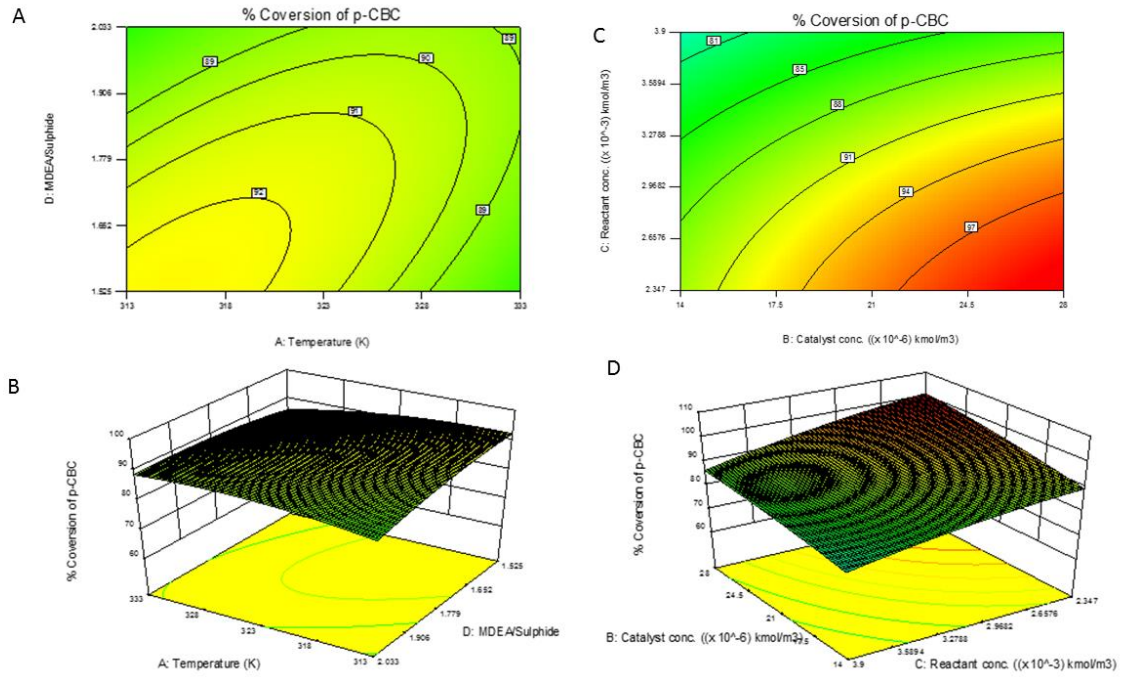


Figure 5.5: The effect and interaction of different independent variables for the response % conversion of p-CBC (A) Counter-plot of interaction of MDEA/Sulfide ratio and temperature (B) 3D surface plot of interaction of MDEA/Sulfide ratio and temperature (C) Counter-plot of interaction of reactant concentration and catalyst concentration (D) 3D surface plot of interaction of reactant concentration and catalyst concentration.

5.3.6. Effect of model components on the selectivity of BPCBS and their interaction

For the BPCBS selectivity, all the variables are significant as the p-value is less than 0.01 except for the temperature of the reaction as its p-value is 0.379 which is greater than 0.01. From the coefficient estimate, the effect of different variables on the responses i.e. conversion of p-CBC and selectivity of BPCBS can be understood. If the coefficient estimate is positive for a variable, then the response increase with an increase in the value of the variable and vice versa. So from the from the coefficient estimate it is clear that catalyst concentration, Reactant concentration, temperature and MDEA/Sulfide ratio have a positive effect on the conversion of p-CBC. The catalyst concentration plays a vital role in the enhancement of the selectivity of BPCBS.

The study of 3D plot and counter-plot (Fig. 5.6 and Fig. 5.7) gives us a clearer interpretation of the effect of variables interaction on p-CBC conversion and BPCBS

selectivity. 3D surface plot helps to understand the effect of single or combined effect of variables on the response, on the other hand, counter-plot helps to know the major interaction of variables with the response on the basis of nature of curve i.e. circular or elliptical.

The increase in BPCBS selectivity was observed with increase in the concentration of the catalyst, reactant concentration, temperature and the MDEA/Sulfide ratio where the temperature has the least impact on the selectivity. The reason for the specific behavior of BPCBS selectivity due to the concentration of the catalyst and the MDEA/Sulfide ratio is same as stated for conversion of p-CBC. But with an increase in reactant concentration, the selectivity of BPCBS increases because as the undesired product i.e. p-CBM recombines with the excess unreacted p-CBC to form more BPCBS. Temperature plays an insignificant role in the selectivity of BPCBS.

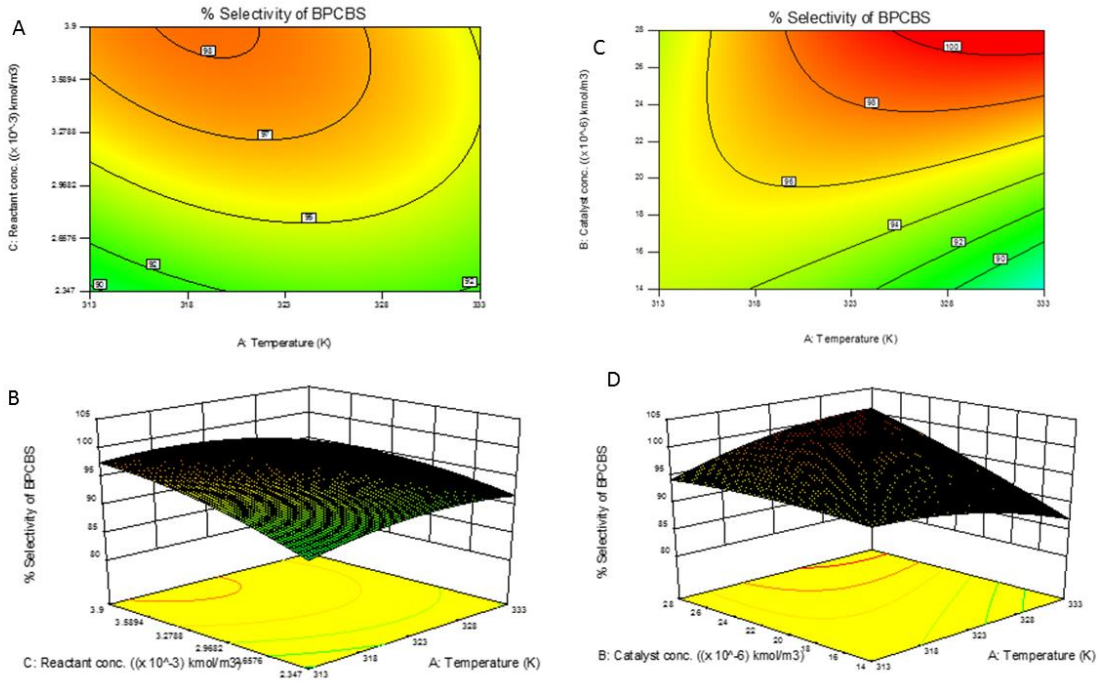


Figure 5.6: The effect and interaction of different independent variables on the response % selectivity of BPCBS (A) Counter-plot of interaction of reactant concentration and temperature (B) 3D surface plot of interaction of reactant concentration and temperature (C) Counter-plot of interaction of catalyst concentration and temperature (D) 3D surface plot of interaction of catalyst concentration and temperature.

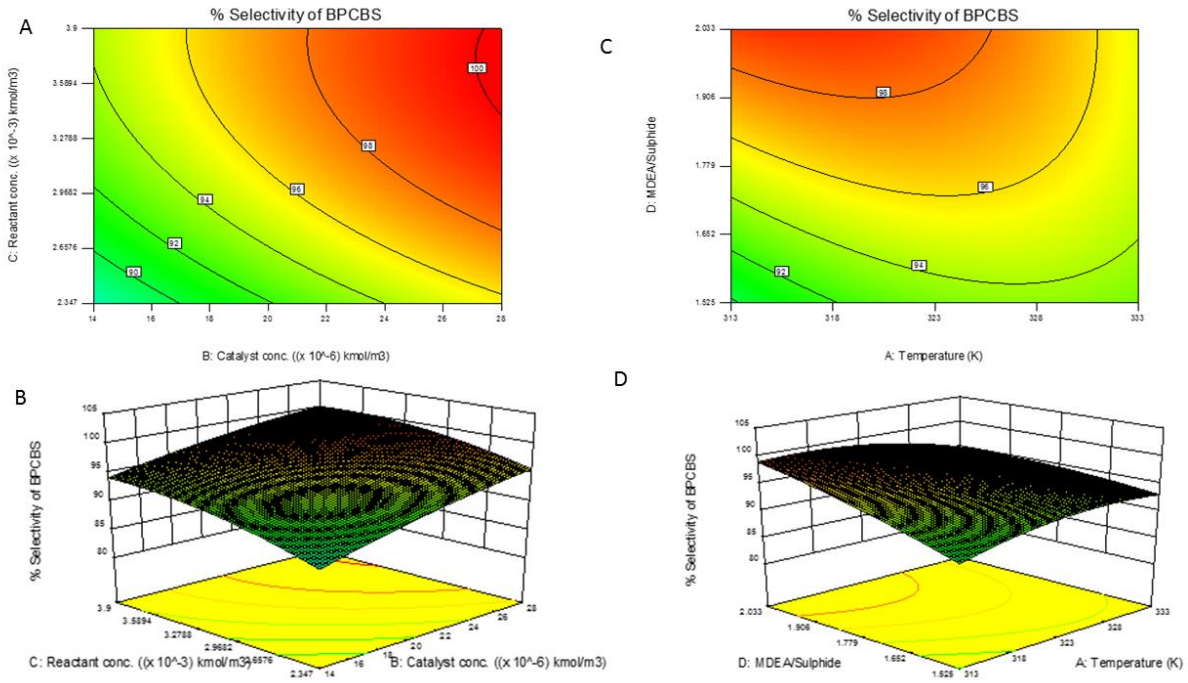


Figure 5.7: The effect and interaction of different independent variables on the response % selectivity of BPCBS (A) Counter- plot of interaction of reactant concentration and catalyst concentration (B) 3D surface plot of interaction of reactant concentration and catalyst concentration (C) Counter-plot of interaction of MDEA/Sulfide ratio and temperature (D) 3D surface plot of interaction of MDEA/Sulfide ratio and temperature.

5.3.7. Dual optimization of % conversion of p-CBC and % selectivity of BPCBS

The primary objective of this investigation and use of RSM is to optimize the values of effecting parameters in order to maximize the conversion of p-CBC and the selectivity of BPCBS. Optimization has been done to minimize the production of side product p-CBM and to make the process of synthesis more viable. Based on design model, the software develops various solutions of optimum response. Best solutions with maximum desirability were tabulated for each set of optimized variables and response. For a particular optimization solution with their corresponding desirability values, the typical desirability plot is shown in Fig. 5.8. The individual desirability for the maximum conversion of p-CBC and selectivity of BPCBS is shown as 0.99 and 0.99 when the values of all variables are in range. For different criteria like minimum catalyst concentration, minimum temperature and for both the values of the variable and the respective desirability is represented in Table 5.5. The optimum values of the different variable for the maximum p-CBC conversion and BPCBS selectivity, are as follows: temperature: 327.34 K, Catalyst concentration: 2.8×10^{-5} kmol/m^3, reactant concentration: 2.468×10^{-3} kmol/m^3, MDEA/Sulfide ratio: 2.033.

Table 5.5: Optimization of reaction condition based on the criteria [a]

Criteria	*Cata. conc. × 10^6 ($kmol/m^3$)*	*React.conc. × 10^3 ($kmol/m^3$)*	*Temp. (K)*	*MDEA/Sulfide ratio*	*Conversion p-CBC (%)*	*Selectivity of BPCBS (%)*	*Desirability*
Maximum BPCBS selectivity and p-CBC conversion	28.00	2.468	327.34	2.033	99.95	100.00	0.999
Maximum BPCBS selectivity	27.74	3.801	323.05	1.973	85.49	100.00	1.000
Maximum BPCBS selectivity and p-CBC conversion and minimum catalyst conc.	15.986	2.835	317.50	1.934	87.884	96.16	0.726
Maximum BPCBS selectivity and p-CBC conversion and minimum Temp.	28.00	2.653	313.87	2.033	96.504	96.625	0.884
Maximum BPCBS selectivity and p-CBC conversion, minimum catalyst conc. and minimum Temp.	14.883	2.825	313.00	1.908	85.989	94.816	0.778

[a] Limit of % p-CBC conversion = 50 – 100% ; Limit of % BPCBS selectivity = 50 – 100%.

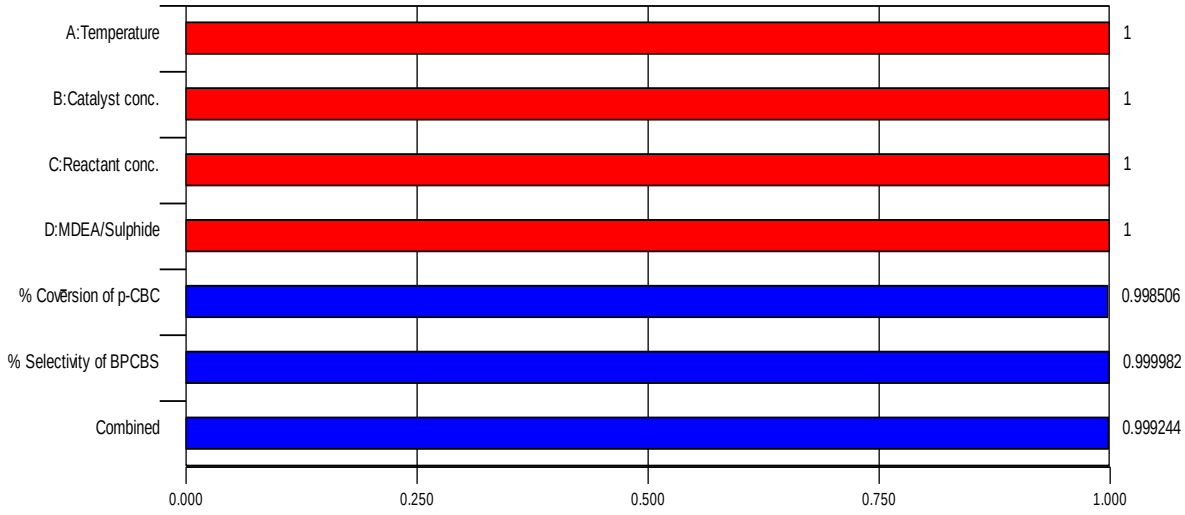


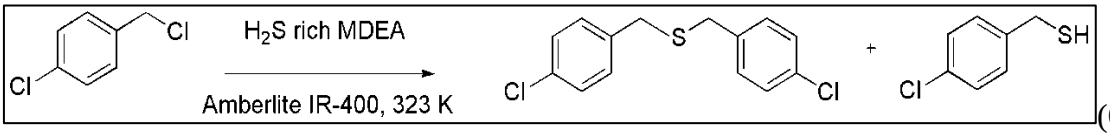
Figure 5.8: Desirability plot for the optimized solution.

CHAPTER 6

Solvent-free Synthesis of Bis-(p-chlorobenzyl) Sulfide under Liquid-Liquid-Solid Catalysis

6.1. Introduction

The investigation is carried out to synthesize aromatic thioether using solid phase transfer catalyst which can be further reused and H_2S laden MDEA in the absence of a solvent. So here in the process, we are using p-chlorobenzyl chloride as an organic reactant which will react with the sulphiding agent H_2S rich MDEA in the presence of polymer-supported catalyst Amberlite IR-400 without using any organic solvent. As the organic solvent is hazardous in nature, it leads to severe disposal problems besides this solvents are expensive and used in large volumes, so the solvent-free synthesis of any organic compound is an economical process. Two products were identified namely BPCBS and p-chlorobenzyl mercaptan (p-CBM) by GC-MS. In the present investigation, we have studied the effect of different parameters like catalyst, sulfide, reactant and MDEA concentration as well as the temperature of the system. The catalyst was reused up to 3 times to study its recoverability. The overall reaction is as shown in the equation (6.1).



(6.1)

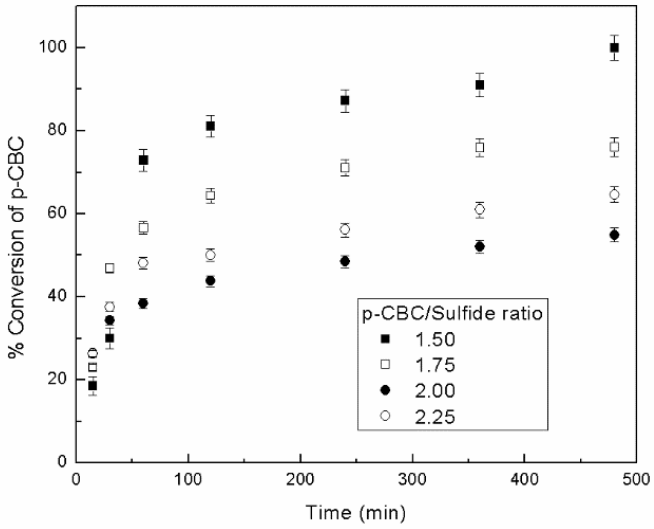
6.2. Result and discussion

6.2.1. Sensitivity study

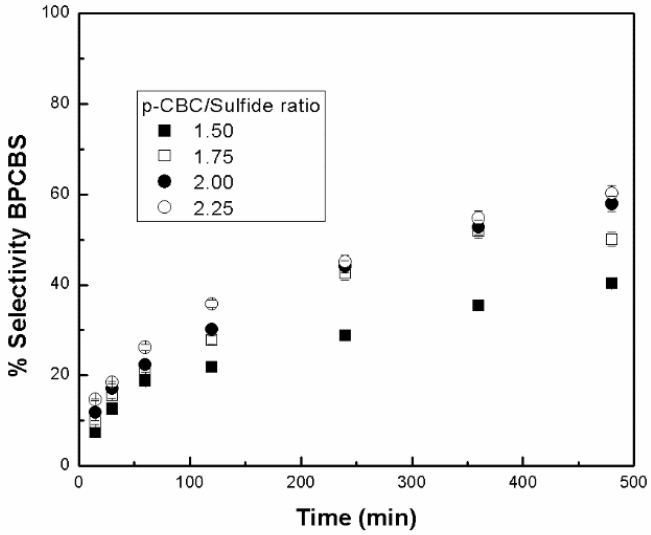
For the study of the effect of different parameters on the conversion p-CBC and selectivity of BPCBS, we will vary one parametric condition keeping other conditions constant (OFAT process). The typical parameters taken have been chosen from the literature and previous study (Maity et al. 2006; Maity et al. 2009; Pradhan and Sharma 1992).

6.2.1.1. Effect of p-CBC/sulfide ratio

From the preliminary study of the same variation, we observed an insignificant effect of reactant concentration change on the conversion p-CBC and selectivity of BPCBS. It was because of very high concentration of reactant as compared to sulfide concentration, and in this case, the sulfide concentration becomes a limiting reagent and stops the reaction at the middle. So from the literature, we found the range of p-CBC/Sulfide ratio to study its effect on the kinetics of the reaction (Sujit Sen 2011). Thus we varied the p-CBC/Sulfide ratio in the range of 1.5-2.25 kmol/m^3 and its effect on the conversion of p-CBC and selectivity of BPCBS was observed as shown in Fig. 6.1.



(a)



(b)

Fig 6.1: The effect of reactant concentration on (a) conversion of p-CBC and (b) selectivity of BPCBS.
Thermochemical condition: Volume of aqueous phase: 6×10^{-5} m^3 each, temperature: 323 K, MDEA concentration: 3.05 kmol/m^3, stirring speed: 1500 rpm, catalyst concentration: 0.195 kmol/m^3, sulfide concentration: 2.0 kmol/m^3.

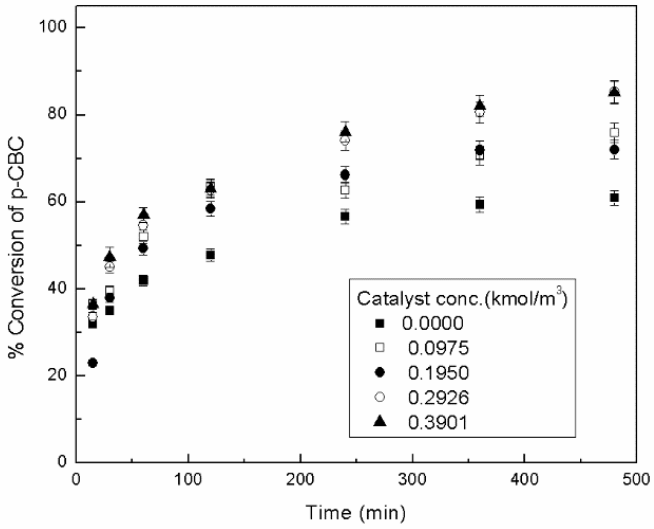
From the variation, we observed that up on increasing the reactant concentration the conversion of the reactant decreases Fig. 6.1 (a) on the contrast the variation increases the selectivity of BPCBS Fig. 6.1 (b). When the reactant concentration increases but the S^{2-} and HS^{-} ions are same, so the sulfide ions get limited, and the excess reactant remains unreacted, this leads to decrease in conversion of p-CBC. But the selectivity of the product BPCBS increases as the intermediate side product p-CBM combines with the excess reactant to form the final product BPCBS. The optimum value of p-CBC concentration for the further study was taken as 1.75 kmol/m^3.

6.2.1.2. Effect of the catalytic concentration

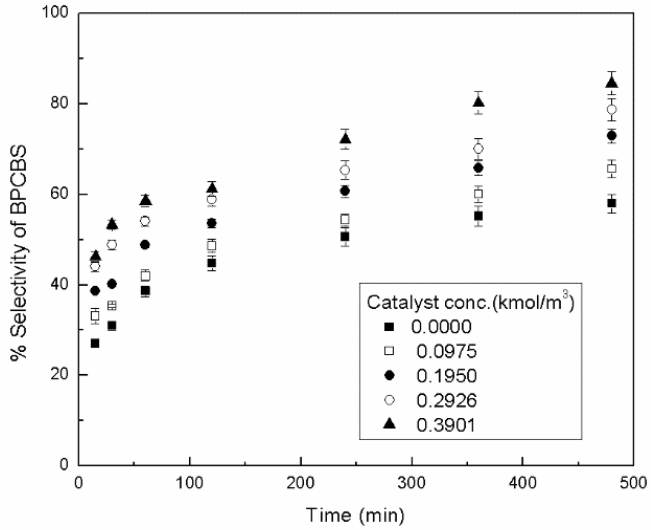
For the study of the effect of concentration of the catalyst, we varied the catalytic concentration in the range 0-0.3901 kmol/m^3. We observed that with an increase in catalyst concentration the conversion of p-CBC Fig. 6.2 (a) and selectivity of BPCBS Fig. 6.2 (b) increases. The ions S^{2-} and HS^{-} form active intermediates QSQ and QSH of catalyst that combines with p-CBC to form BPCBS and p-CBM. Upon increasing catalyst concentration, the concentration of these intermediate increases and hence the conversion of p-CBC and selectivity of BPCBS also increases (Sujit Sen 2011). For the further study, we have taken the catalyst concentration as 0.2926 kmol/m^3.

6.2.1.3. Effect of sulfide concentration

In aqueous phase, H_2S, H_2O, and MDEA react with each other to form ion pairs of S^{2-} and HS^{-} ions which are accountable for total sulfide concentration of the aqueous phase. When the sulfide concentration increases, HS^{-} ion concentration increases more that S^{2-} ions which lead to the formation of more intermediate product i.e. p-CBM than the final product (Maity et al. 2009). From the experimental analysis also we found the supporting results. As shown in the Fig 6.3 the increase in sulfide concentration leads to increase in conversion of p-CBC (Fig. 6.3 (a)) but decrease in the selectivity of BPCBS (Fig. 6.3 (b)). The increase in the conversion of p-CBC is due to the limited concentration of reactant as compared to sulfide concentration. The typical value of the sulfide concentration for most of the reaction was taken to be 2.0 kmol/m^3.



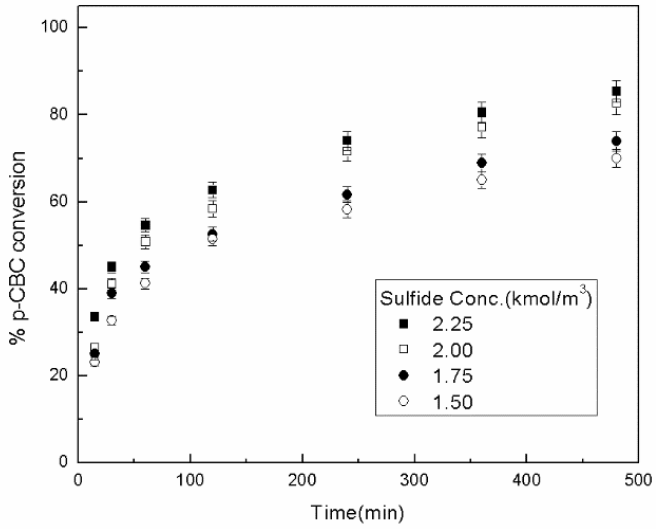
(a)



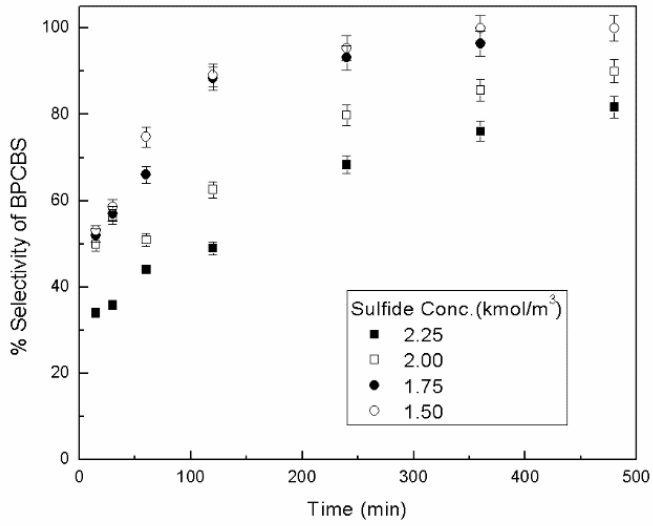
(b)

Fig 6.2: The effect of catalyst concentration on (a) conversion of p-CBC and (b) selectivity of BPCBS.

Thermochemical condition: Volume of aqueous phase: 6×10^{-5} m^3 each, temperature: 323 K, MDEA concentration: 3.05 $kmol/m^3$, stirring speed: 1500 rpm, reactant concentration: 1.75 $kmol/m^3$, sulfide concentration: 2.0 $kmol/m^3$.



(a)



(b)

Fig 6.3: The effect of sulfide concentration on (a) conversion of p-CBC and (b) selectivity of BPCBS.

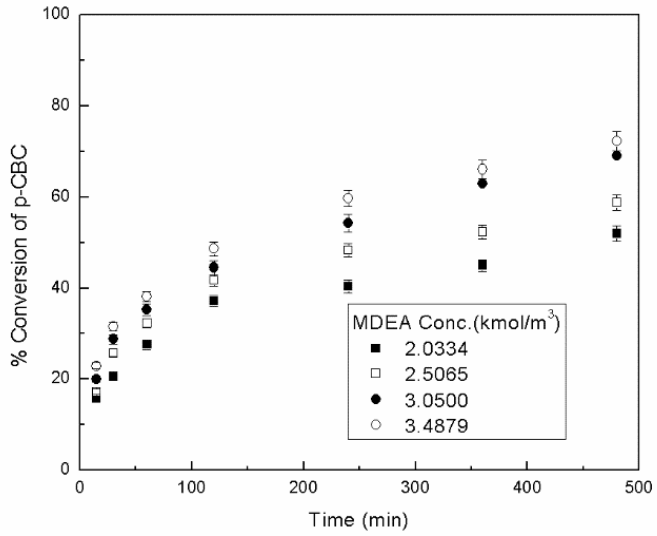
Thermochemical condition: Volume of aqueous phase: 6×10^{-5} m^3 each, temperature: 323 K, MDEA concentration: 3.05 kmol/m^3, stirring speed: 1500 rpm, reactant concentration: 1.75 kmol/m^3, catalyst concentration: 0.2926 kmol/m^3.

6.2.1.4. Effect of MDEA concentration

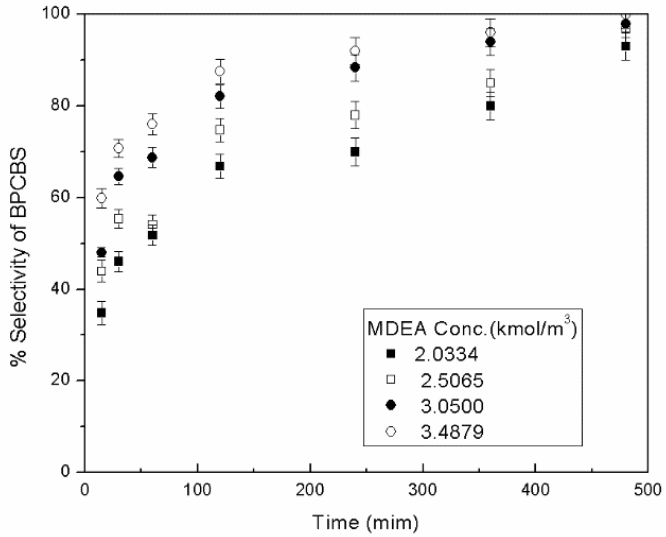
In our present work MDEA merely plays the role of an absorbent and has hardly any effect on the reaction mechanism but it still plays a role in the kinetics of the reaction. The reaction between H_2O-H_2S-MDEA forms ionic equilibria from where ions go to the interface of the catalyst to react with the organic substrate. As the concentration of MDEA increases, the equilibrium shift towards the product and more ionic products are formed which employees more conversion of reactant as well as selectivity of BPCBS. From the Fig. 6.4 it is clearly visible that with the increase in the concentration of MDEA, the conversion of p-CBC and selectivity of BPCBS increase. The typical value of the concentration of MDEA was taken to be 3.05 kmol/m^3.

6.2.1.5. Effect of the reaction temperature

All our reactions were carried out in an isothermal water bath with PID control to maintain the uniform temperature in which we can change the temperature of the reaction. Mostly the rate of reaction increases with increase in temperature except for exothermic reactions. From collision theory, with an increase in temperature more molecules collide with each other with sufficient energy to cause the successful reaction. From Arrhenius theory, at a higher temperature, the molecules gain sufficient energy to reach the activation energy and start the reaction. From the Fig. 6.5 it is clearly visible that the conversion of p-CBC and selectivity of BPCBS are increasing with increase in temperature. Both of the theories supports the experimental behavior of the reaction.



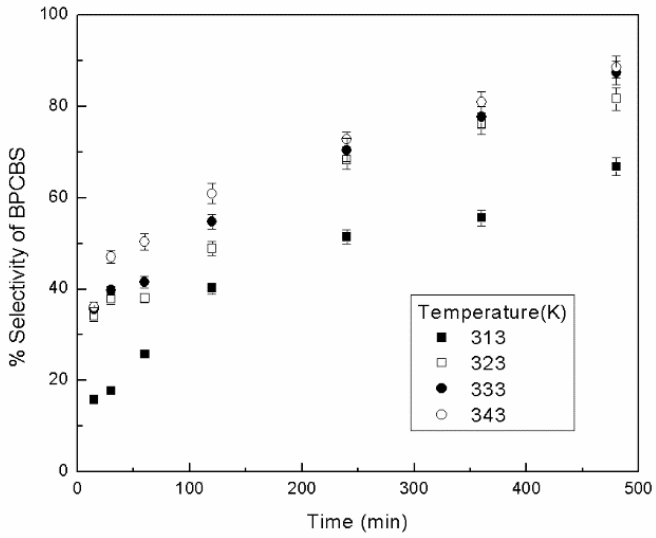
(a)



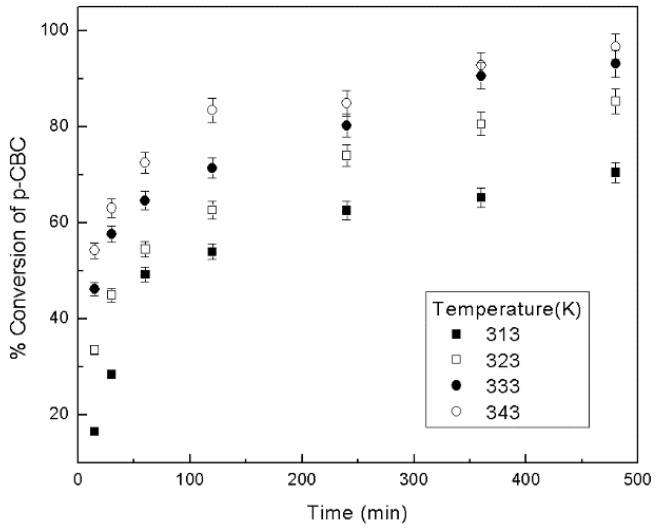
(b)

Fig 6.4: The effect of MDEA concentration on (a) conversion of p-CBC and (b) selectivity of BPCBS.

Thermochemical condition: Volume of aqueous phase: 6×10^{-5} m^3 each, temperature: 323 K, Sulfide concentration: 1.5 kmol/m^3, stirring speed: 1500 rpm, reactant concentration: 1.75 kmol/m^3, catalyst concentration: 0.2926 kmol/m^3.



(a)



(b)

Fig 6.5: The effect of temperature concentration on (a) conversion of p-CBC and (b) selectivity of BPCBS.

Thermochemical condition: Volume of aqueous phase: 6×10^{-5} m^3 each, MDEA concentration: 3.05 kmol/m^3, Sulfide concentration: 2.0 kmol/m^3, stirring speed: 1500 rpm, reactant concentration: 1.75 kmol/m^3, catalyst concentration: 0.2926 kmol/m^3.

From the Arrhenius plot (Fig. 6.5) between the ln (initial rate of reaction) and 1/T (temperature), the activation energy was found to be 8.795 kJ/mol.

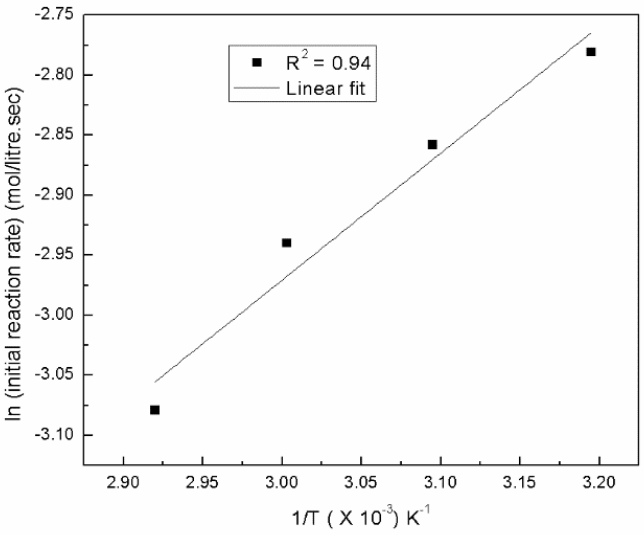


Fig. 6.6: Arrhenius plot ln (initial rate of reaction) vs. 1/T (temperature)

6.2.1.6. Reusability of the catalyst

The PTC, which is impregnated on a solid support, can be regenerated and reused as they are immiscible in both the phases so can easily be filtered and reused. The PTC are expensive hazardous in nature hence causes disposal problems. The actual reason behind the synthesis of polymer-supported catalyst was to use the catalyst more than one times and make it more economically viable. The PTC employed in the present work is Amberlite IR-400, which was washed, regenerated and reused up to 3 times to study its effect on the conversion of the reactant. For this study, all the catalysts after each run of experiments were collected in an air-tight container then it was washed several times with water followed by acetone. Acetone is a good solvent which dissolves all the organic trace on the catalyst. For the regeneration of the catalyst, the catalyst was mixed with the NaCl solution then again washed with distilled water to dissolve excess NaCl.

The regenerated catalyst was used three times and conversion of p-CBC, which was 85 % for the fresh catalyst, decreased to 76%. As shown in the figure Fig.6.6. As all the

sites of the catalyst are could not get regenerated as well as loss of catalyst also happen while regenerating it, the decrease in the conversion of reactant was observed.

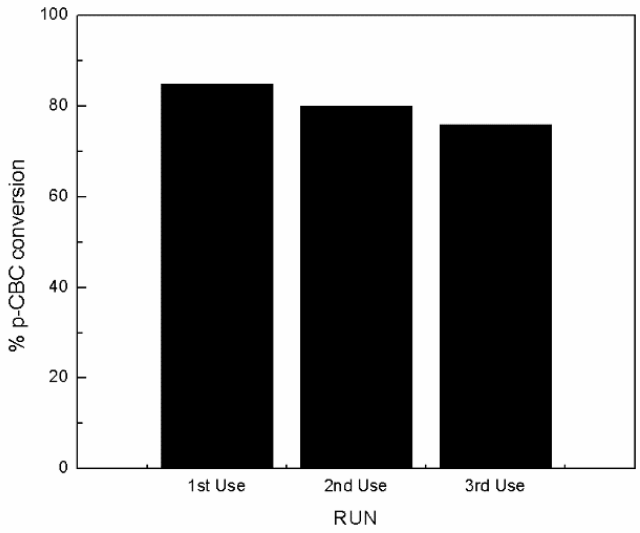


Fig 6.7: The effect of reusability of the catalyst on conversion of p-CBC.

Thermochemical condition: Volume of aqueous phase: 6×10^{-5} m^3 each, temperature: 323 K, MDEA concentration: 3.05 kmol/m^3, Sulfide concentration: 2.0 kmol/m^3, stirring speed: 1500 rpm, reactant concentration: 1.75 kmol/m^3, catalyst concentration: 0.2926 kmol/m^3.

CHAPTER 7

Conclusions and Future work

7.1 Introduction

The main purpose of the complete study is to capture and utilize highly poisonous gas H_2S in synthesizing value added chemicals like aromatic thioether which is also achieved. The main aim of the synthesis is to find its green route of synthesis, i.e., by using a reusable catalyst or in the absence of solvent and to study the effect of different variable one at a time or two simultaneously. But there are many unexplored works that can be done in the same field as the use of different absorbent of H_2S, synthesis of catalyst and study or the system can be made single stage process.

7.2 Conclusions

Some major conclusions and achievements of Chapter 4:

- The aromatic thioether bis-(p-chlorobenzyl) sulfide is synthesized with 100% selectivity at some point of reaction, using H_2S laden MDEA and p-chlorobenzyl chloride in the presence of solvent toluene and PTC tributylmethylammonium chloride polymer bound under L-L-S mode of catalysis.
- The sensitivity of the synthesis is studied with respect to the concentration of catalyst, sulfide, MDEA, and p-CBC, reusability, stirring speed and temperature.
- The catalyst is compared with other soluble, and insoluble catalysts under same reaction conditions and the polymer-supported catalyst is found to give the best result as compare to other PTC.
- In the study of the temperature effect, Arrhenius plot ln (initial rate of reaction) vs. 1/T (temperature) is also plotted from the slop of which the activation energy of the reaction was also calculated to be 34.86 kmol/m^3.
- In the effect of intensity of stirring, it is observed that there is no mass transfer effect if we go beyond 1000 rpm.
- The general kinetic model is developed which is found to make a good agreement between the predicted and experimental values of conversion of p-CBC.

Some major conclusions and achievements of Chapter 5:

- In this process of investigation, the synthesis of BPCBS is successfully achieved by using p-CBC and H_2S laden MDEA using tributylmethylphosphonium chloride polymer-supported catalyst as PTC L-L-S mode of reaction.
- Using RSM with CCD the model for the system is developed by estimation of regression coefficients.
- The model is found fit for dual responses i.e. p-CBC conversion and BPSBS selectivity for the given range of the variables.
- 3D surface plot and the counter-plots are used to understand the effect of different parametric conditions on the reaction and their interaction with each other.
- The optimization of the reaction condition is also done to achieve maximum p-CBC conversion and BPCBS selectivity using desirability function.

Some major conclusions and achievements of Chapter 6:

- Bis-(p-chlorobenzyl) sulfide is synthesized with 100% selectivity at some point of reaction, using H_2S laden MDEA and p-chlorobenzyl chloride in the absence of any solvent and PTC Amberlite IR-400, under the L-L-S mode of catalysis.
- The sensitivity of the synthesis is studied w.r.t concentration of catalyst, sulfide, MDEA, and p-CBC, reusability and temperature.
- The catalyst is reused up to 3 times with very little depression in its activity
- In the study of the temperature effect, Arrhenius plot ln (initial rate of reaction) vs. 1/T (temperature) is also made from the slop of which the activation energy of the reaction is also calculated to be 8.795 kmol/m^3.

7.3 Future recommendation

This is just half way achieved in making the process green, economical and more industrially adoptable. There are many unfolded areas which can be explored in the future:

- Use of some other alkanolamines, such as MDEA, MEA, DIPA, and DGA along with mixed alkanolamines like MDEA with DIPA can be used for selective removal of H_2S.

- The effect of pH of H_2S-rich alkanolamines, the addition of other anions as a co-catalyst (for example NaCl) and adding up alkali (for example NaOH) on the

conversion of p-CBC and selectivity of BPCBS are some future recommended sensitivity study.

- The present reaction scheme can be applied to synthesize other thioethers from reactants having active methylene (-CH_2) group. Substituted benzyl halide or other heterocyclic having active – CH_2X (X = Cl, Br, I) can also be tested for the synthesis of thioethers.

- The present work was done in two stage; the first stage deals with the making of the H_2S-rich alkanolamine solution and the second stage deals with the synthesis of aromatic thioethers. The reactions can be turned into a single step synthesis by charging the H_2S gas through a mixture of alkanolamines and the reactants in a single reactor so that simultaneous chemisorption and reaction can take place.

- The present scheme doesn't allow reuse of spent amine solution again. After the reaction, the lean amine solution can be reused to absorb more H_2S and then can be reused as a sulfiding agent again. It can better be achieved in a continuous flow reactor and not in a stirred batch reactor we have used here.

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DISSEMINATION

Dissemination

International Journals

1. **Preeti Jha,** Ujjal Mondal, Devipriya Gogoi, Gaurav Singh and Sujit Sen, "Novelties of selective triphasic synthesis of bis-(p-chlorobenzyl) sulfide using hydrogen sulfide and reusable phase transfer catalyst'', *J. Mol. Catal. A Chem*. 2016, 418-419, 30-40
2. Gaurav Singh, Priya G. Nakade, Dorothy Chetia, **Preeti Jha**, Ujjal Mondal, Saroj Kumari and Sujit Sen, "Kinetics and mechanism of phase transfer catalyzed synthesis of aromatic thioethers by H_2S-rich methyldiethanolamine'', *J. Ind. Eng. Chem*. 2016, 37, 190-197.
3. Gaurav Singh, Priya G. Nakade, Pratik Mishra, **Preeti Jha**, Sujit Sen, Ujjal Mondal, "Kinetic investigation on liquid–liquid–solid phase transfer catalyzed synthesis of dibenzyl disulfide with H_2S-laden monoethanolamine", *J. Mol. Catal. A Chem*. 2015, 411, 78–86.
4. **Preeti Jha**, Sujit Sen, "Dual optimization in liquid-liquid-solid phase transfer catalyst synthesis of organic thioethers using Hydrogen sulfide" *Under review*.
5. **Preeti Jha**, Sujit Sen, "Solvent free synthesis of organic thioethers using Hydrogen sulfide under liquid-liquid-solid phase transfer catalysis" *Manuscript under preparation.*

International Conferences

1. Gaurav Singh, Priya G. Nakade, **Preeti Jha**, Devipriya Gogoi, Sujit Sen, "Parametric Studies in Synthesis of Aromatic Thioethers using Hydrogen Sulfide under Liquid-Liquid Phase Transfer Catalyst", Indian Chemical Engineering Congress (**CHEMCON-2014**), Punjab University, Chandigarh, India, December 27-30, 2014.

RESUME

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